FLUCTUATIONS OF TRACE CONTAMINANTS IN SEWAGE TREATMENT PLANTS

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No. 1

FLUCTUATIONS OF TRACE CONTAMINANTS IN SEWAGE TREATMENT PLANTS

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1.0 INTRODUCTION

Millions of dollars have been, and continue to be, spent by government and industry to control the discharge of contaminants to the receiving water environment. These efforts have resulted in improvements in water quality in terms of nutrients and conventional contaminants. However, new chemicals are continually developed by industry in response to the demands of modern society. These chemicals and their process by-products find their way into the sewer system. Increasingly sophisticated analytical methodologies can detect the presence of trace contaminants at concentrations of less than 1 ug/L. Health effects research and biological testing techniques continue to identify the impacts of long-term exposure to low level concentrations of these trace contaminants.

National attention has been drawn to the issue of trace contaminants in the environment by recent media reports of deteriorating water quality in the Great Lakes Basin. These media reports refer, often in sensational terms, to a wide variety of organic chemicals being discharged from large municipal water pollution control plants (WPCPs) and diverse industrial sources into the Great Lakes and their tributary rivers. Many of the trace contaminants identified have proven or suspected long-term human health impacts.

In Ontario approximately 12,000 industries discharge into the 400 municipal treatment facilities. In contrast, only 400 industries discharge their treated wastewaters directly to surface water (Ho, 1986). The municipal water pollution control plant thus represents the last line of defense against discharge of large quantities of contaminants in wastewater to the natural environment. Conventional plants depend to a large extent on biological processes and were designed to remove conventional contaminants such as BOD_5, suspended solids and pathogenic microorganisms. Recent research has shown that biological treatment systems can also achieve a high degree of trace contaminant control when operated under stable conditions and after the microbial biomass has had an opportunity to acclimate to the contaminants present in the wastewater. However, in full-scale WPCPs, steady state conditions do not exist and the biological processes are exposed to highly variable input loadings of a wide variety of contaminants. The degree of variability which can be tolerated by conventional biological processes and the dynamic response of these processes to transient conditions is presently unknown.

Municipalities and regulatory agencies are aware of the need to protect the treatment facility against upsets due to discharges of toxics to the sanitary sewer system. This protection is afforded by the imposition of sewer use regulations on industrial dischargers. However, these sewer use bylaws rarely address trace organic contaminants specifically, due to the lack of definitive information with respect to the impact of these contaminants on the treatment processes.

In response to this basic lack of understanding of the dynamics of trace contaminant fluctuations in wastewater treatment plants, CANVIRO Consultants received funding to investigate the dynamic behaviour of trace contaminants in full-scale pollution control plants.

The program is multi-phased, consisting of an initial technical review of the literature concerning trace contaminants

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in wastewater treatment facilities. In addition to the technical review, this project investigates the response of full-scale and laboratory-scale activated sludge systems to dynamic fluctuations of trace contaminants in raw wastewater. The monitoring programs will help to identify the need for improved strategies, such as biological process control on industrial pretreatment programs, for management of trace contaminant levels in final effluents of treatment plants subjected to fluctuating influent concentrations.

This report is the technical review of the literature concerning trace contaminants in wastewater treatment plants and collection systems. The review is based upon full-scale treatment plant data received from provincial and state authorities, and data retrieved from published literature.

Trace contaminant concentrations in raw wastewater, final effluents, sludges and internal recycle streams have been compiled and analyzed for concentrations, frequency of occurrence and variability, where possible. Particular attention has been paid to data identifying the dynamic fluctuations or variability of trace contaminants in wastewater treatment systems. Contaminant removals have been summarized, and the mechanisms responsible for trace contaminant removal have been identified. Mathematical models describing the removal mechanisms and used for predicting contaminant reductions have been assessed. Concentrations of trace contaminants in wastewater collection systems have been reviewed; models predicting contaminant levels in sewer systems have also been discussed.

The purpose of this review is to characterize the dynamic fluctuations of trace contaminants in wastewater treatment collection systems, so that management strategies required to adequately control trace contaminant levels in wastewater treatment plant discharges can be identified.

2.0 PROGRAM OBJECTIVES

The specific objectives of the Technical Review are as follows:

- To conduct a critical review of the technical literature and to compile the available information with respect to trace contaminants as it pertains to the following specific areas:
  - i) the variability of industrial discharges to municipal sewer systems;
  - ii) the variability of the raw influent to municipal water pollution control plants;
  - iii) the quality of internal recycle streams, such as digester supernatant, sludge dewatering liquors and incinerator scrubber water, and the impact of these recycle streams on process performance; and,
  - iv) the dynamic behaviour of wastewater treatment unit processes, particularly biological treatment processes, with respect to trace contaminants.
- To define the implications of the compiled information on the management of trace contaminants in municipal sewer systems and wastewater treatment plant effluents.
- To identify specific areas where critical information is presently lacking and modify the work program of subsequent phases to address these areas.

3.0 TRACE CONTAMINANT CHARACTERIZATION DATA

3.1 Trace Contaminants in Raw Wastewater

Contaminant concentrations in raw wastewater have been compiled from data received from provincial or state environmental authorities, and from the technical literature. Primarily post 1980 have been used to try to avoid outdated information (specifically with respect to improved detection limits). Ontario data are drawn from the Toronto area and Niagara region treatment plants. Concentration data were also received from Ohio, Indiana, Illinois and Wisconsin state authorities.

The data have been examined to evaluate not only which contaminants are present, but the magnitude of the concentrations, the frequency of observation, and where possible, the variability of the contaminants in raw wastewater at full-scale treatment facilities.

Metro Toronto monitored the presence of trace organic contaminants in its four WPCPs in 1985. Single grab samples of raw sewage and final effluent were collected once each week for four weeks at each treatment plant (Metro Toronto, 1986). The concentrations of purgeable compounds in the 4 Metro Toronto pollution control plants are summarized in Table 1. Toluene was the contaminant present at highest concentrations, with mean levels of 347 ug/L at the Highland Creek plant, and 139 ug/L at the Main plant. Purgeable compounds were fewer in number and observed less frequently at the North Toronto plant than at the other plants. The variability of the purgeables was high with relative standard deviations (RSDs) frequently greater than 100 percent of the mean value.

In the acid extractable organics group for the Metro Toronto treatment plant influents, phenol and cresols were present at the highest concentrations as shown in Table 2. The variability of these compounds was also high, particularly at Humber and Highland Creek plants (e.g. RSD values ranged from 70 to 200 percent of the mean values).

Phthalate esters, chlorinated benzenes and naphthalene were the most frequently observed base/neutral extractables in Metro Toronto raw wastewaters (Table 3). Of these compounds, bis(2-ethylhexyl) phthalate was present at the highest concentrations in all plants. The Humber and North Toronto plants had fewer compounds in this group than the Main or Highland Creek plants. Contaminant concentration variability was frequently high, partly because the levels were close to the detection limit.

Pesticides were observed most frequently in the North Toronto plant relative to the other plants, although in almost all cases, the concentrations were very low (Table 4). The herbicide 2,4-D was present in all the plants except Humber, at a mean concentration above 1 ug/L.

The concentrations of trace inorganics in raw wastewater at three Niagara region treatment plants are summarized in Table 5. Zinc and copper were observed most frequently at all plants, but lead was the dominant metal at Welland while cadmium was found in the highest concentration of all metals at Niagara Falls. Considerable variability in the concentrations was observed, but as with the Toronto data, the sample size was not large.

TABLE 1. CONCENTRATIONS OF PURGEABLE COMPOUNDS IN METRO TORONTO WPCP INFLUENTS (METRO TORONTO, 1986)

PURGEABLE COMPOUNDS	TORONTO MAIN				NORTH TORONTO				HIGHLAND CREEK				HUMBER			
	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (\$)	OCCURRENCE (\$)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (\$)	OCCURRENCE (\$)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (\$)	OCCURRENCE (\$)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (\$)	OCCURRENCE (\$)
1,1-Dichloroethylene	4.5	2.8	63	100	ND	--	--	0	17.0	7.91	46.4	100	9.4	6.6	70	100
Dichloromethane	45.1	21.3	47.3	100	8.2	3.6	44	100	14.4	5.49	38.1	100	54.8	14.1	25.8	100
1,1-Dichloroethane	4.7	9.5	200	25	ND	--	--	0	1.1	1.7	150	50	0.8	1.0	130	50
Chloroform	2.5	2.8	110	75	3.8	2.3	61	100	2.6	0.4	15	100	10.7	4.5	43	100
1,1,1-Trichloroethane	5.6	3.8	69	75	ND	--	--	0	59.9	24.6	41.1	100	23.4	10.7	45.7	100
Benzene	ND	--	--	0	0.1	0.3	200	25	ND	--	--	0	0.1	0.3	200	25
Bromodichloromethane	ND	--	--	0	ND	--	--	0	ND	--	--	0	ND	--	--	0
Trichloroethylene	2.4	2.3	96	75	ND	--	--	0	5.8	6.8	120	100	3.5	0.41	12	100
Toluene	139	35.8	25.6	100	1.3	0.9	71	100	347	581	167	100	69	88	130	100
Tetrachloroethylene	6.6	2.1	31	100	ND	--	--	0	7.9	5.6	70	100	4.4	2.0	45	100
Ethyl benzene	22.0	6.6	29.9	100	1.1	1.2	110	100	17	18	110	100	17	15	87	100
p- and m-Xylene	63.2	15.6	24.6	100	1.8	0.27	15	100	53.9	54.6	101	100	56.2	44.5	79.1	100
o-Xylene	42.8	13.8	32.3	100	1.4	0.48	35	100	44.7	46.4	104	100	34.9	29.6	85.0	100
1,4-Dichlorobenzene	4.8	0.83	17	100	0.8	0.5	70	75	6.0	2.5	43	100	6.0	1.2	20	100
1,2-Dichlorobenzene	4.3	1.7	40	100	0.6	1.3	200	25	0.3	0.5	200	25	3.8	2.9	77	100

$\bar{X}$ = Arithmetic Mean
S.D. = Standard Deviation of Mean
RSD = Relative Standard Deviation (\$ of Mean Value)
Occurrence = No. of Detections/No. of Tests
No. of grab samples= 4

TABLE 2. CONCENTRATIONS OF ACID EXTRACTABLE ORGANICS IN METRO TORONTO WPCP INFLUENTS (METRO TORONTO, 1986)

ACID EXTRACTABLE	TORONTO MAIN				NORTH TORONTO				HIGHLAND CREEK				HUMBER			
	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)
Phenol	48.9	35.5	72.6	75	13.2	9.9	75	100	68.5	101	147	100	79.1	90.4	114	100
2,4-Dimethylphenol	2.7	4.7	180	50	9.4	3.9	41	100	2.0	2.7	140	50	ND	--	--	0
p-Chloro-m-cresol	1.8	2.0	120	50	3.7	6.1	160	50	ND	--	--	0	16.7	11.4	68.4	100
2,4-Dichlorophenol	0.8	0.5	67	75	0.8	0.5	70	75	0.8	0.5	70	75	0.3	0.5	200	25
Pentachlorophenol	2.6	3.2	120	50	1.4	1.2	87	75	0.7	1.3	200	25	ND	--	--	0
o-Cresol	18.1	11.8	65.3	100	9.0	10.3	120	75	6.4	8.6	130	75	5.3	7.3	140	50
m-Cresol	18.1	12.5	68.9	75	9.1	15.2	170	50	6.1	7.1	120	75	201	252	125	100
p-Cresol	417.6	268.4	64.3	100	93.6	79.4	84.9	100	337	417	124	100	279	298	107	100
2,4,6-Trichlorophenol	ND	--	--	0	0.3	0.5	200	25	0.3	0.5	200	25	ND	--	--	0

$\bar{X}$ = Arithmetic Mean
S.D. = Standard Deviation of Mean
RSD = Relative Standard Deviation (% of Mean Value)
Occurrence = No. of Detections/No. of Tests
No. of grab samples= 4

TABLE 3. CONCENTRATIONS OF BASE/NEUTRAL EXTRACTABLE ORGANICS IN METRO TORONTO WPCP INFLUENTS (METRO TORONTO, 1986)

BASE/NEUTRAL EXTRACTABLES	TORONTO MAIN				NORTH TORONTO				HIGHLAND CREEK				HUMBER			
	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)
1,4-Dichlorobenzene	11.2	5.7	50.9	100	7.0	4.3	61	100	11.1	1.59	14.4	100	17.1	8.3	48	100
1,2-Dichlorobenzene	12.9	11.5	89.3	100	9.6	4.4	46	100	2.1	2.2	100	75	8.7	9.1	100	75
Naphthalene	6.1	4.6	76	100	1.5	1.2	79	75	2.0	1.6	82	75	4.7	5.2	110	75
Acenaphthene	0.1	0.3	200	25	0.1	0.3	200	25	ND	--	--	0	ND	--	--	0
Acenaphthylene	0.1	0.3	200	25	0.1	0.3	200	25	ND	--	--	0	ND	--	--	0
Diethyl phthalate	10.7	3.9	36.5	100	9.0	3.8	42	100	17.3	7.19	41.6	100	8.9	3.3	37	100
9H Fluorene	0.5	0.7	140	50	0.4	0.3	70	75	0.4	0.3	70	75	ND	--	--	0
Phenanthrene	1.2	0.53	45.2	100	0.8	0.4	50	100	0.8	0.9	100	75	0.5	0	0	100
Anthracene	0.3	0.3	100	50	ND	--	--	0	0.1	0.3	200	25	ND	--	--	0
Di-n-butyl phthalate	19.6	98.8	50.6	100	1.6	1.6	100	75	32.6	48.4	149	100	15.7	12.3	78.4	100
Fluoranthene	0.9	0.8	90	100	ND	--	--	0	0.9	1.4	160	50	0.4	0.3	70	75
Pyrene	1.4	0.7	52	100	0.5	0.6	120	50	1.2	1.1	94	75	0.8	0.5	70	75
Chrysene	0.5	0.6	120	50	ND	--	--	0	0.3	0.5	200	25	ND	--	--	0
Benzo(a)anthracene	0.3	0.3	100	50	ND	--	--	0	0.3	0.5	100	25	ND	--	--	0
Bis(2-ethylhexyl) phthalate	134	58.3	43.4	100	63.8	66.5	104	100	69.4	36.6	52.8	100	85.5	19.1	22.4	100
Benzo(k)fluoranthene	1.3	2.0	150	75	ND	--	--	0	0.3	0.5	200	25	ND	--	--	0
Benzo(b)fluoranthene	0.4	0.3	70	75	ND	--	--	0	0.3	0.5	200	25	ND	--	--	0
Benzo(a)pyrene	ND	--	--	0	ND	--	--	0	0.3	0.5	200	25	ND	--	--	0

$\bar{X}$ = Arithmetic Mean
S.D. = Standard Deviation of Mean
RSD = Relative Standard Deviation (% of Mean Value)
Occurrence = No. of Detections/No. of Tests
Number of grab samples = 4

TABLE 4. CONCENTRATIONS OF PESTICIDES IN METRO TORONTO WPCP INFLUENTS (METRO TORONTO, 1986)

PESTICIDE	TORONTO MAIN				NORTH TORONTO				HIGHLAND CREEK				HUMBER			
	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)
Hexachlorobenzene	ND	--	--	0	ND	--	--	0	0.005	0.01	200	25	ND	--	--	0
alpha-BHC	ND	--	--	0	0.01	0.03	200	25	ND	--	--	0	ND	--	--	0
beta-BHC	ND	--	--	0	0.1	0.3	200	25	ND	--	--	0	ND	--	--	0
gamma-BHC	0.07	0.08	100	50	0.02	0.03	164	50	0.055	0.097	180	50	0.02	0.04	200	25
4,4' DDD	ND	--	--	0	0.04	0.09	200	25	ND	--	--	0	ND	--	--	0
4,4'-DDE	ND	--	--	0	0.23	0.46	200	25	ND	--	--	0	ND	--	--	0
Dieldrin	ND	--	--	0	ND	--	--	0	ND	--	--	0	ND	--	--	0
alpha-Endosulfan	ND	--	--	0	ND	--	--	0	ND	--	--	0	ND	--	--	0
Oxychlordane	ND	--	--	0	0.01	0.03	200	25	ND	--	--	0	ND	--	--	0
gamma-Chlordane	0.01	0.02	120	50	ND	--	--	0	ND	--	--	0	ND	--	--	0
Mirex	0.005	0.01	200	25	ND	--	--	0	ND	--	--	0	ND	--	--	0
Atrazine	ND	--	--	0	ND	--	--	0	ND	--	--	0	ND	--	--	0
2,4-D	2.1	4.2	200	25	1.7	2.0	120	50	1.0	2.0	200	25	ND	--	--	0

$\bar{X}$ = Arithmetic Mean
S.D. = Standard Deviation of Mean
RSD = Relative Standard Deviation (% of Mean Value)
Occurrence = No. of Detections/No. of Tests
No. of grab samples = 4
ND = Not Detected

TABLE 5. CONCENTRATIONS OF TRACE INORGANICS IN NIAGARA REGION WPCP INFLUENTS (MOE, Undated)

INORGANIC	WELLAND					FORT ERIE					NIAGARA FALLS				
	n	$\bar{X}$ (mg/L)	S.D. (mg/L)	RSD (%)	OCCURRENCE (%)	n	$\bar{X}$ (mg/L)	S.D. (mg/L)	RSD (%)	OCCURRENCE (%)	n	$\bar{X}$ (mg/L)	S.D. (mg/L)	RSD (%)	OCCURRENCE (%)
Silver	5	0.010	0.014	140	40	4	ND	--	--	0	3	ND	--	--	0
Arsenic	6	0.004	0.005	140	50	4	0.0003	0.0005	200	25	4	0.0003	0.0005	200	25
Cadmium (ug/L)	7	ND	--	--	0	4	0.001	0.001	120	0	4	0.025	0.050	200	25
Chromium	7	0.020	0.015	77	71	4	0.008	0.010	120	50	4	0.006	0.006	120	50
Copper	7	0.054	0.031	57	100	4	0.03	0.03	86	75	4	0.05	0.01	28	100
Mercury (ug/L)	7	0.180	0.290	160	57	4	0.13	0.03	26	100	4	0.14	0.034	25	100
Nickel	7	0.002	0.005	260	14	4	0.001	0.002	200	25	4	0.001	0.003	200	25
Lead	7	0.31	0.35	110	71	4	0.01	0.01	140	50	4	0.004	0.007	200	25
Zinc	7	0.14	0.090	64	100	3	0.07	0.02	31	100	4	0.095	0.0058	6.1	100
Cyanide	7	0.0002	0.0003	120	0	4	0.001	0.003	200	25	4	0.04	0.07	190	50

n = No. of samples
$\bar{X}$ = Arithmetic Mean
S.D. = Standard Deviation of Mean
RSD = Relative Standard Deviation (% of Mean Value)
Occurrence = No. of Detections/No. of Tests
ND = Not Detected

Samples consist of 1 to 3 daily 8 hr composites combined to one final composite

TRACE CONTAMINANT CHARACTERIZATION DATA

The concentrations of purgeable organics in the raw wastewater entering Niagara (Ontario) region water pollution control plants are reported in Table 6. With the exception of dichloromethane (methylene chloride), most compounds were found at mean concentration of less than 10 ug/L. At the Fort Erie Anger Avenue plant, toluene had a mean concentration of 12 ug/L. The variability of the samples was high, due to the limited number of samples and concentrations near the detection level.

Pesticide concentrations in the Niagara region treatment plants are reported in Table 7. Lindane (gamma-BHC) was the most frequently observed pesticide in the wastewaters. Other than Lindane, PCB mixtures Aroclor 1248 and 1254 were present in the highest concentrations.

Metal concentrations in the influent to several Ohio wastewater treatment plants are reported in Table 8. The data result from only one or two 24-hour composite samples, and so is not possible to assess the in-plant variability of the metals. Zinc was typically the metal present at the highest level in the 5 plants. Cyanide was present at high levels in Marion wastewater. Dayton influent was higher in most metals than the other Ohio treatment plant influents.

TABLE 8. TRACE INORGANIC CONCENTRATIONS IN SELECTED OHIO WASTEWATER TREATMENT PLANT INFLUENTS (BULZAN, 1986)

INORGANIC	CONCENTRATION (ug/L)				
	MARION	ALLIANCE	LIMA	WAPAKONETA	DAYTON
Arsenic	5	ND	<5	<4	5
Cadmium	16	<10	2	4	10
Chromium	ND	30	34	50	390
Copper	42	90	62	58	160
Mercury	ND	ND	<0.2	<0.2	<2
Nickel	33	ND	70	43	170
Lead	ND	<50	13	66	<50
Zinc	104	200	171	97	410
Cyanide	560	<10	5	<10	50

ND = Not Detected

No. of Samples = 1 or 2 24-hr composites

Concentrations of trace organic contaminants in selected Ohio treatment plants are reported in Table 9. These data also result from only one or two 24-hour composite samples, an are subject to the same limitations as the metals data. Purgeables and phthalate esters were most commonly observed in all the plants. The raw wastewaters of Lima, Alliance and Toledo contained few organics. Some wastewaters such as Cleveland Southerly and Westerly plants contained groupings of non-priority pollutants at elevated levels.

Mean monthly concentrations of metals in the raw wastewater of five Indiana treatment plants are reported in Table 10. The data have not always been reported each month, and consequently it is difficult to determine if monthly variation is significant. Exceptionally high levels of zinc and

TABLE 6. CONCENTRATIONS OF PURGEABLE COMPOUNDS IN NIAGARA REGION WPCP EFFLUENTS (MOE Undated)

COMPOUNDS	WELLAND					FORT ERIE					NIAGARA FALLS				
	n	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	n	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	n	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)
Dichloromethane	2	ND	--	--	0	3	53	92	170	33	2	88	116	130	100
Chloroform	2	1.3	1.8	140	50	3	9.9	8.8	89	100	3	9.7	9.0	93	100
1,1,1-Trichloroethane	2	0.10	0.14	140	50	3	4.8	4.8	99	100	3	0.2	0.3	170	33
1,1,2-Trichloroethane	2	0.15	0.21	140	50	3	3.5	6.1	170	33		NA	--	--	—
Cis-1,2-dichloroethylene	1	0.10	--	--	100	1	0.3	--	--	100		NA	--	--	—
Trichloroethylene	2	0.10	0.14	140	50	3	0.1	0.2	170	33	3	0.07	0.1	170	33
Tetrachloroethylene	2	0.20	0.28	140	50	3	6.4	5.1	79	100	3	4.3	6.7	157	67
Benzene	2	0.05	0.71	140	50	3	0.2	0.3	170	33	3	0.07	0.1	170	33
1,2-Dichlorobenzene	2	1.7	2.3	140	50	3	4.1	3.7	91	67	3	0.6	1.0	170	33
1,3-Dichlorobenzene	2	ND	--	--	0	2	4	5	140	50	3	1.0	1.7	170	33
1,4-Dichlorobenzene		NA	--	--	—	2	2	2	140	50	3	ND	--	--	0
Ethyl benzene	2	0.10	0.14	140	50	3	0.1	0.2	170	33	3	0.03	0.06	170	33
Toluene	2	3.0	4.2	140	50	3	12	16	130	100	3	0.8	0.7	90	67
Chlorotoluenetrifluoride	1	6.0	--	--	100		NA	--	--			NA	--	--	—
o-Xylene	2	0.3	0.4	140	50	3	0.3	0.5	170	33	3	0.1	0.2	170	33
m-Xylene	2	0.4	0.5	140	50	3	5	6	120	100	3	0.1	0.2	170	33
p-Xylene	2	0.3	0.4	140	50	3	0.3	0.5	170	33	3	0.1	0.2	170	33
Chlorodibromomethane	2	ND	--	--	0	3	ND	--	--	0	3	5.0	8.7	170	33
Dichlorobromomethane	2	ND	--	--	0	3	ND	--	--	0	3	3.7	6.4	170	33
1,1-Dichloroethane	2	ND	--	--	0	3	10.3	13.8	130	67	3	0.02	0.03	170	33
1,2-Dichloroethane	2	ND	--	--	0	3	ND	--	--	0	3	0.03	0.06	170	33
Bromoform		NA	--	--	—	3	0.5	0.8	170	33		NA	--	--	--
1,1-Dichloroethylene		NA	--	--	—	3	0.07	0.1	170	33	3	ND	--	--	0
1,2-t-Dichloroethylene	2	ND	--	--	0	2	ND	--	--	0	2	ND	--	--	0
Chlorobenzene		NA	--	--	—	3	.03	.06	170	33	3	0.07	0.1	170	33

NA = Not Analyzed

$\bar{X}$ = Arithmetic Mean

S.D. = Standard Deviation of Mean

RSD = Relative Standard Deviation (% of Mean Value)

Occurrence = No. of Detections/No. of Tests

n = Number of samples

ND = Not Detected

Samples consist of 1 to 4 grabs reduced to a single composite just before analysis

TABLE 7. CONCENTRATIONS OF PESTICIDE/PCBs IN NIAGARA REGION WPCP INFLUENTS (MOE, Undated)

COMPOUND	WELLAND					FORT ERIE					NIAGARA FALLS				
	n	$\bar{X}$ (ng/L)	S.D. (ng/L)	RSD (%)	OCCURRENCE (%)	n	$\bar{X}$ (ng/L)	S.D. (ng/L)	RSD (%)	OCCURRENCE (%)	n	$\bar{X}$ (ng/L)	S.D. (ng/L)	RSD (%)	OCCURRENCE (%)
alpha-BHC	3	1.7	2.9	173	33	3	1.3	1.5	110	67	3	0.3	0.6	170	33
gamma-BHC	3	19	8.1	42	100	3	6.7	4.5	67	100	3	3.0	5.2	170	33
alpha-Chlordane	3	3.3	5.8	170	33	3	10	10	100	67	3	2.0	3.5	170	33
gamma-Chlordane	3	4.0	6.9	170	33	3	12	12	100	67	3	1.7	2.9	170	33
Dieldrin	3	1.3	2.3	170	33	3	1.3	2.3	170	33		NA	--	--	—
Hexachlorobenzene	3	8.3	14	170	33		NA	--	--	--	3	0.7	1.2	170	33
Aroclor 1248	3	13	23	170	33	3	ND	--	--	0		NA	--	--	—
beta-BHC (mg/L)	3	ND	--	--	0		NA	--	--	—		NA	--	--	—
Endosulfan sulfate	3	ND	--	--	0		NA	--	--	--		NA	--	--	--
Heptachlor		NA	--	--	—	3	ND	--	--	0		NA	--	--	--
p,p-DDE		NA	--	--	—	3	0.3	0.6	170	33	3	1.0	1.0	100	33
Aroclor 1254		NA	--	--	—	3	23	40	170	33	3	40	35	88	67
Methoxychlor		NA	--	--	—		NA	--	--	--	3	ND	--	--	0
Endosulfan I		NA	--	--	—		NA	--	--	—	3	ND	--	--	0
Oxychlordane		NA	--	--	—		NA	--	--	—	3	ND	--	--	0
p,p-DDD		NA	--	--	—		NA	--	--	--	3	ND	--	--	0
p,p-DDT		NA	--	--	—		NA	--	--	--	3	ND	--	--	0
Archlor 1260		NA	--	--	—		NA	--	--	—	3	ND	--	--	0

NA = Not Analyzed

$\bar{X}$ = Arithmatic Mean

S.D. = Standard Deviation of Mean

RSD = Relative Standard Deviation (% of Mean Value)

Occurrence = No. of Detections/No. of Tests

n = Number of samples

ND = Not Detected

Samples consist of 1 to 3 daily 8 hr composites combined to one final composite

TABLE 9. CONCENTRATIONS OF ORGANIC CONTAMINANTS IN SELECTED OHIO WASTEWATER INFLUENTS (BULZAN, 1986)

ORGANIC CONTAMINANT	CONCENTRATION (ug/L)									
	WAPAKONETA	LIMA	TOLEDO	DAYTON	ALLIANCE	CLEVELAND EASTERLY	CLEVELAND SOUTHERLY	CLEVELAND WESTERLY	COLUMBUS JACKSON PIKE	COLUMBUS SOUTHERLY
1,1,1-Trichloroethane	10	<1		44.8		15	6	11		
1,1,2,2-Tetrachloroethane						29	7			
1,2 Diphenylydrazine						28				
1,2-t-Dichloroethylene	2.2			41						
1,4-Dichlorobenzene	1.1									
1-Octenal, 2-Butyl								23		
1-Pentyn-3-ol, 3-Methyl								67		
1-Propene, 3-Ethenyloxy							18			
2-Heptene, 1-Chloro						280	26			
2-Hexenoic acid, 2-Hexenyl ester								48		
2-Pentenol, 2,4-Dimethyl							270			
2-Propen-1-ol, 2-Methyl							31			
4-Chloro-3-methylphenol							55	110		
4-Methyl phenol				23						
4-Nitrophenol						168				
Acetone							74			
Aldehyde or Ketone, 5-6-Carbons								54		
Anthracene			24.5							
Benzene										
Benzo(a)anthracene	5.6									
Bis-(2-chlorethoxy) methane							48			
Bis-(2-chlordiisopropyl) ether						390				
Bis-(2-ethylhexyl) phthalate	82	75.9	25.5	28.3					17	20
Butylbenzyl phthalate							66		50	
Carbon disulphide								1600		
Carbon tetrachloride				18						

TABLE 9. CONCENTRATIONS OF ORGANIC CONTAMINANTS IN SELECTED OHIO WASTEWATER INFLUENTS (BULZAN, 1986) (cont'd)

	CONCENTRATION (ug/L)									
ORGANIC CONTAMINANT	WAPAKONETA	LIMA	TOLEDO	DAYTON	ALLIANCE	CLEVELAND EASTERLY	CLEVELAND SOUTHERLY	CLEVELAND WESTERLY	COLUMBUS JACKSON PIKE	COLUMBUS SOUTHERLY
Chloroform	4			19.5	12				12	3.3
Chrysene	6.1									
Cyclopropane, 1-Ethylidene, Bis							51			
Di-n-butyl phthalate	24									
Di-n-octyl phthalate	10		7	13						
Dichlorobenzenes				10						
Diethyl phthalate	6							15		
Dimethyl naphthalene								38		
Ethane, 1,2-Diethoxy								140		
Ethyl benzene				38.5		27	5	9	7.5	5.3
Furan, 3-Methyl								32		
g-BHC							19	58		
Heptadecane - 4 Propyl								11		
Hexadecanoic acid 2-oxo- Methyl ester								10		
Isophorone						38		12		
Methylene chloride	260			25	40	53	75	100	45	44
n-Nitrosodiphenylamine							110			
Naphthalene				7		36	11			
Phenanthrene	1.7									
Phenol	11			79.8			61	610	50	50
Pyrene	3.5						18			
Tetrachloroethylene	20			64.3		32	14		44	
Toluene	6.3		26	3 40		11	13	9	20	12
Trichloroethylene	3.8			1 60				26	150	190
Xylene							46	120		

No. of samples = 1 or 2 24-hr composites

TABLE 10. MONTHLY AVERAGE INORGANIC CONTAMINANT CONCENTRATIONS IN INDIANA TREATMENT PLANT INFLUENT SAMPLES (BRUMFIELD, 1986)

INORGANIC CONTAMINANT	CITY	MONTHLY AVERAGE METAL CONCENTRATIONS (ug/L)												
		JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEPT	OCT	NOV	DEC	GRAND AVG.
Cadmium	Columbus	0	0	0	0	0	0	10	0	10	0	NR	NR	2
	Crawfordsville	10	10	NR	NR	NR	NR	NR	NR	NR	10	10	10	10
	Elkhart	NR	20	10	10	10	15	20	10	15	10	15	10	13
	Michigan City	NR	NR	15	15	15	15	16	NR	NR	NR	NR	NR	15
	Speedway (Indianapolis)	1	1	NR	NR	NR	NR	NR	NR	10	10	2	2	4
Chromium	Columbus	120	140	170	140	190	110	100	180	180	140	NR	NR	150
	Crawfordsville	20	25	NR	NR	NR	NR	NR	NR	NR	30	35	10	24
	Elkhart	NR	100	50	30	25	60	85	65	20	90	75	70	61
	Michigan City	NR	NR	190	230	190	360	470	NR	NR	NR	NR	NR	290
	Speedway	150	40	NR	NR	NR	NR	NR	NR	30	90	15	170	80
Copper	Columbus	70	90	110	90	140	140	160	150	140	220	NR	NR	130
	Crawfordsville	20	20	NR	NR	NR	NR	NR	NR	NR	38	37	15	26
	Elkhart	NR	110	120	150	170	310	160	220	400	230	160	120	200
	Michigan City	NR	NR	110	135	135	115	110	NR	NR	NR	NR	NR	120
	Speedway	90	10	NR	NR	NR	NR	NR	NR	50	30	20	60	40
Mercury	Columbus	0.6	0	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	0.2
	Crawfordsville	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	-
	Elkhart	NR	0.4	0.3	0.2	0.2	0.2	0.2	0.5	NR	NR	NR	NR	0.3
	Michigan City	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	-
	Speedway	0.5	0.5	NR	NR	NR	NR	NR	NR	0.5	0.5	0.5	0.5	0.5

TABLE 10. MONTHLY AVERAGE INORGANIC CONTAMINANT CONCENTRATIONS IN INDIANA TREATMENT PLANT INFLUENT SAMPLES (BRUMFIELD, 1986) (cont'd)

INORGANIC CONTAMINANT	CITY	MONTHLY AVERAGE METAL CONCENTRATIONS (ug/L)												
		JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEPT	OCT	NOV	DEC	GRAND AVG.
Nickel	Columbus	140	130	140	120	200	80	60	80	130	70	NR	NR	120
	Crawfordsville	10	10	NR	NR	NR	NR	NR	NR	NR	180	55	22	55
	Elkhart	NR	100	100	45	30	85	60	65	140	60	75	50	73
	Michigan City	NR	NR	45	150	120	20	60	NR	NR	NR	NR	NR	79
	Speedway	10	10	NR	NR	NR	NR	NR	NR	10	10	10	10	10
Lead	Columbus	40	50	50	40	40	30	40	40	50	60	NR	NR	40
	Crawfordsville	10	15	NR	NR	NR	NR	NR	NR	NR	10	80	30	29
	Elkhart	NR	55	90	50	70	50	60	35	10	45	60	40	51
	Michigan City	NR	NR	10	35	75	35	15	NR	NR	NR	NR	NR	34
	Speedway	10	10	NR	NR	NR	NR	NR	NR	100	75	25	30	42
Zinc	Columbus	230	290	230	210	260	250	270	290	280	300	NR	NR	260
	Crawfordsville	10	15	NR	NR	NR	NR	NR	NR	NR	180	170	130	100
	Elkhart	NR	140	300	310	150	270	160	480	330	250	200	80	240
	Michigan City	NR	NR	1780	1840	1410	2000	2270	NR	NR	NR	NR	NR	1860
	Speedway	210	60	NR	NR	NR	NR	NR	NR	130	90	100	110	120
Cyanide	Columbus	20	20	20	NR	NR	NR	NR	NR	NR	NR	NR	NR	20
	Crawfordsville	10	15	NR	NR	NR	NR	NR	NR	NR	120	20	10	35
	Elkhart	NR	10	20	20	20	30	10	10	10	20	20	10	20
	Michigan City	NR	NR	3150	7330	1200	13900	1180	NR	NR	NR	NR	NR	5430
	Speedway	15	20	NR	NR	NR	NR	NR	NR	10	20	15	20	17

NR = Not Recorded

No. of samples ranges from 0 to 17

Type of sample not specified

cyanide were reported for the Michigan City plant. In the April and June samples for this city, cyanide levels were 7,730 and 13,900 ug/L, respectively. Crawfordsville, on the other hand, had very low levels of all metals. Between plant variability metal concentrations is significant.

Annual concentrations of cadmium, chromium and copper in two Milwaukee WI wastewater treatment plants are reported in Table 11. At the South Shore plant, cadmium concentrations began to decline in 1978 from much higher levels, while a decline in copper and chromium levels began in 1980. At the Jones Island plant, cadmium levels began to decrease in 1981, but copper and chromium levels remained relatively constant. The raw wastewaters at both treatment plants have unusually high mean chromium concentrations of greater than 2,000 ug/L. Much of the chromium in the raw wastewater of these plants is due to leather tanning. The decline in chromium concentrations is partly a result of a switch from chrome tanning to other tanning methods, and a poor economic climate for the leather industry (Kleinert, 1987). Although Wisconsin adopted the proposed state/federal pretreatment regulation in 1983, Milwaukee restricted the discharge of cadmium by industrial sources to municipal sewers in 1981 (Kleinert, 1987). The decline in cadmium in both plants appears to result in part from municipal pretreatment programs. Reduced concentrations of chromium and copper in the raw wastewater of the South Shore plant in 1983, may also be a result of the state/federal pretreatment program. Metal concentrations between 1983 and 1986 have continued to decline as a result of pretreatment (Kleinert, 1987).

Annual influent metal concentrations at the Madison Wisconsin wastewater treatment plant are summarized in Table 12. Zinc was present at the highest concentration, with a mean concentration of 320 ug/L.

The concentrations of trace organic contaminants in selected Wisconsin wastewater treatment plants are reported in Table 13. The two contaminants noted most regularly were toluene and bis(2-ethylhexyl) phthalate. Specific individual compounds were higher at some plants than at others (e.g. phenol at Jones Island, tetrachloroethylene at South Shore, 1,1,1-trichloroethane at Kenosha, toluene and butylbenzyl phthalate at Green Bay).

Mean concentrations of organic contaminants from sampling programs in Illinois are summarized in Table 14. Purgeables and phthalate esters occurred most frequently in the wastewater. Naphthalene and phenol were the most frequently occurring base/neutral and acid extractable compounds, respectively. Toluene was the compound with the highest mean concentration. PAHs other than naphthalene were detected only occasionally at low concentrations.

Organic contaminant concentrations in the raw wastewater of two Chicago treatment plants in July and August of 1984 are reported in Table 15. At the Calumet plant, aromatic hydrocarbons such as benzene, toluene and ethyl benzene predominated, whereas at the West-Southwest plant, chlorinated solvents such as trichloroethylene, 1,1,1-trichloroethane and methylene chloride, as well as toluene were the major contaminants. PAHs and dichlorobenzene concentrations were less than 1 ug/L. Few acid extractable compounds were detected; only phenol was observed above 2 ug/L in the west side of the West Southwest plant. Pesticide concentrations were too low for detection by the GC/MS method of analysis.

TRACE CONTAMINANT CHARACTERIZATION DATA

TABLE 11. ANNUAL INFLUENT CONCENTRATIONS OF SELECTED HEAVY METALS IN MILWAUKEE WASTEWATER TREATMENT PLANTS (KLEINERT, 1986)

METAL	YEAR	JONES ISLAND	SOUTH SHORE
		INFLUENT (ug/L)	INFLUENT (ug/L)
Cadmium	1975	49	31
	1976	51	24
	1977	57	20
	1978	40	12
	1979	51	13
	1980	52	11
	1981	35	10
	1982	26	9
	1983	23	7
	Grand Mean	43 ± 12	15 ± 8
Chromium	1975	3,160	3,550
	1976	2,620	3,180
	1977	2,220	2,210
	1978	2,520	2,720
	1979	2,630	2,380
	1980	2,440	1,740
	1981	1,980	2,170
	1982	1,560	1,440
	1983	2,220	1,130
	Grand Mean	2370 ± 452	2280 ± 788
Copper	1975	194	628
	1976	247	574
	1977	190	854
	1978	199	627
	1979	199	679
	1980	193	230
	1981	202	164
	1982	164	181
	1983	187	127
	Grand Mean	197 ± 21.8	451 ± 274

No. and type of samples not specified

TABLE 12. ANNUAL MEAN INFLUENT METAL CONCENTRATIONS IN MADISON WISCONSIN (KLEINERT, 1986)

METAL	YEAR	MEAN INFLUENT CONCENTRATION (ug/L)
Cadmium	1979	2.6
	1980	1.9
	1981	2.0
	1982	8.0
	Grand Mean	3.6
Chromium	1979	23
	1980	36
	1981	45
	1982	53
	Grand Mean	39
Copper	1979	51
	1980	65
	1981	69
	1982	73
	Grand Mean	65
Mercury	1979	1.4
	1980	1.6
	1981	1.7
	1982	1.5
	Grand Mean	1.6
Nickel	1979	31
	1980	37
	1981	17
	1982	15
	Grand Mean	25
Lead	1979	20
	1980	30
	1981	23
	1982	19
	Grand Mean	23
Zinc	1979	320
	1980	340
	1981	300
	1982	310
	Grand Mean	320

No. and type of samples not specified

TABLE 13. ORGANIC CONTAMINANTS IN SELECTED WISCONSIN RAW WASTEWATERS (KLEINERT, 1986)

COMPOUND	CONCENTRATION (ug/L)					
	JONES ISLAND[1]	SOUTH SHORE[1]	RACINE[2]	MADISON[3]	KENOSHA[2]	GREEN BAY[2]
Methylene chloride	20	61	-	50	120	-
1,2-t-Dichloroethylene	7.1	-	27.5	-	-	-
Chloroform	5.6	4.8	14.3	19	-	<1
1,1,1-Trichloroethane	5.4	33	31.9	-	350	18
Trichloroethylene	61	31	31.1	-	-	24
Benzene	4.0	6.8	11.9	-	-	-
Toluene	26	43	13.5	12	20	212
Ethyl benzene	3.7	29	11.1	-	-	-
Tetrachloroethylene	-	128	47.1	-	40	26
1,3-dichloropropylene	-	22	-	-	-	-
Carbon tetrachloride	-	-	5.7	-	-	-
Chlorobenzene	-	-	7.3	-	-	-
Chlorodibromomethane	-	-	3.7	-	-	-
1,1-Dichloroethane	-	-	14.6	-	-	-
1,1-Dichloroethylene	-	-	15.3	-	-	-
1,2-Dichloropropane	-	-	69	-	-	-
Trichlorofluoromethane	-	-	19.1	-	-	-
Phenol	390	-	-	-	-	-
Pentachlorophenol	5.5	-	-	-	-	-
1,3-Dichlorobenzene	-	6.4	-	-	-	-
1,4-Dichlorobenzene	27	3	6.8	-	-	-
1,2-Dichlorobenzene	5.1	1.6	-	-	-	-
Diethyl phthalate	20	12	0.3	-	-	41
Dimethyl phthalate	-	3	-	-	-	-
Di-n-butyl phthalate	11	12	0.3	-	-	10
Butylbenzyl phthalate	7.5	15	-	-	-	146
Bis(2-ethylhexyl) phthalate	81	22	0.4	43	370	37
Naphthalene	7.3	3	-	-	-	-
Fluoranthene	39	5.5	-	-	-	-
Phenanthrene/anthracene	-	8	-	-	-	-
Fluorene	6.9	4.2	-	-	-	-
Pyrene	-	3	-	-	-	-
Chrysene	8.5	-	-	-	-	-
Benzo(a)anthracene	-	2.8	-	-	-	-
Alpha-BHC	-	-	0.05	-	-	-
Dieldrin	-	-	0.12	-	-	-
Heptachlor epoxide	-	-	<0.01	-	-	-
delta-BHC	-	-	-	-	1.2	-
Endosulfan I	-	-	-	-	1.3	-
4,4-DDT	-	-	-	-	4.8	-
Aldrin	-	-	-	-	-	0.11
Hexachlorobenzene	-	-	-	-	-	0.98

1. Jones Island and South Shore data are averages of 2 24-hr composite samples.
2. Racine, Kenosha and Green Bay data are from one 24-hr composite at each wastewater treatment plant.
3. Madison data are from one 24-hr flow proportioned composite sample.

TABLE 14. ORGANIC PRIORITY POLLUTANTS IN ILLINOIS WASTEWATER INFLUENTS (McSWIGGIN, 1986)

COMPOUND	NO. TIMES DETECTED	MEAN CONC'N (ug/L)	COMPOUND	NO. TIMES DETECTED	MEAN CONC'N (ug/L)	COMPOUND	NO. TIMES DETECTED	MEAN CONC'N (ug/L)
Acrolein	0	0	Pentachlorophenol	6	38.1	Hexachlorocyclopentadiene	1	1
Acrylonitrile	0	0	2,4,6-Trichlorophenol	2	6.1	Hexachloroethane	1	7
Benzene	20	9.3	Acenaphthene	2	1.5	Indeno(1,2,3-c,d)pyrene	1	1
Bromoform	2	8.5	Acenaphthylene	1	1	Isophorone	3	8
Carbon tetrachloride	2	2.6	Anthracene	6	1.6	Naphthalene	11	4.1
Chlorodiblamomethane	1	15	Benzidene	1	1	Nitrobenzene	1	2
Chloroethane	2	5.5	Benzo(a)anthracene	3	0.8	n-Nitroso-dimethylamine	1	4
2-chloroethyl vinyl ether	0	0	Benzo(a)pyrene	2	0.8	n-Nitroso-di-n-propylamine	1	1
Chloroform	29	14.7	Benzo(b)fluoranthene	1	3	n-Nitroso-diphenylamine	2	2.6
Dichlorobromomethane	1	0.6	Benzo(g,h,i)perylene	1	2	Phenanthrene	4	0.9
Dichlorodifluoromethane	2	10	Benzo(k)fluoranthene	2	1.6	Pyrene	4	1.5
1,1-Dichloroethane	5	11.1	Bis(2-chloroethoxy)methane	1	20	1,2,4-Trichlorobenzene	2	3
1,2-Dichloroethane	6	14.1	Bis(2-chloroethyl)ether	1	4	Aldrin	8	1.12
1,1-Dichloroethylene	2	0.8	Bis(2-chloroisopropyl)ether	4	16.3	alpha-BHC	12	0.1
1,2-Dichloropropane	0	0	Bis(2-ethylhexyl) phthalate	34	72.2	beta-BHC	5	0.4
1,3-Dichloropropylene	1	1	4-Bromophenyl phenyl ether	1	1	delta-BHC	11	0.1
Ethyl benzene	17	15.7	Butylbenzyl phthalate	15	10	gamma-BHC (Lindane)	9	0.32
Methyl bromide	2	10	2-chloronaphthalene	2	1	Chlordane	4	1.36
Methyl chloride	5	42.2	4-chlorophenyl phenyl ether	1	3	4,4'-DDT	5	4.98
Methylene chloride	27	45.9	Chrysene	2	1.2	4,4'-DDE	5	0.02
1,1,2,2-Tetrachloroethane	3	9.7	Dibenzo(a,h)anthracene	1	6	4,4'-DDD	5	0.016
Tetrachloroethylene	32	55	1,2-Dichlorobenzene	2	2	Dieldrin	6	0.03
Toluene	34	414	1,3-Dichlorobenzene	2	6.5	alpha-Endosulfan	3	0.01
1-2-t-Dichloroethylene	12	44.9	1,4-Dichlorobenzene	11	5.0	beta-Endosulfan	4	0.24
1,1,1-Trichloroethane	23	48.8	3,3'-Dichlorobenzidine	1	18	Endosulfan sulfate	5	0.27
1,1,2-Trichloroethane	2	3.5	Diethyl phthalate	21	28	Endrin	4	0.04
Trichloroethylene	27	27.0	Dimethyl phthalate	2	73.5	Endrin aldehyde	3	0.34
Trichlorofluoromethane	3	1	Di-n-butyl phthalate	20	12.5	Heptachlor	7	0.26
Phenol	9	30	2,4-Dinitrotoluene	1	1	Heptachlor epoxide	7	0.57
2-Chlorophenol	1	21	2,6-Dinitrotoluene	2	1.5	Aroclor 1016	3	0.05
2,4-Dichlorophenol	2	6.5	Di-n-octyl phthalate	3	22	Aroclor 1221	3	0.05
2,4-Dimethyl phenol	3	13	1,2-Diphenylhydrazine	3	1.1	Arcolor 1232	3	0.05
4,6-Dinitro-o-cresol	3	26	Fluoranthene	4	1.4	Aroclor 1242	3	0.05
2,4-Dinitrophenol	2	62.5	Fluorene	2	0.6	Aroclor 1248	4	1.59
2-Nitrophenol	1	17	Hexachlorobenzene	1	4	Aroclor 1254	3	0.44
4-Nitrophenol	1	30	Hexachlorobutadiene	1	5	Aroclor 1260	3	0.84
p-Chloro-m-Cresol	1	13				Toxaphene	3	2.75

Total no. of samples was not specified

TRACE CONTAMINANT CHARACTERIZATION DATA

TABLE 15. CONTAMINANT CONCENTRATIONS IN TWO CHICAGO WASTEWATER TREATMENT PLANT INFLUENTS (MSDGC, 1984)

	CONCENTRATION (ug/L)		
	CALUMET	WEST SOUTHWEST PLANT	
		WEST SIDE	SOUTHWEST
Methylene chloride	1.5	3.8	11.1
1,2-trans-Dichloroethylene	<1	2.4	1.4
Chloroform	3.5	6.6	4.2
1,1,1-Trichloroethane	7.3	15.0	11.1
Trichloroethylene	1.2	48.5	6.9
Benzene	45.3	2.2	<1
Tetrachloroethylene	5.6	9.2	4.4
Toluene	42.4	13.5	15.7
Ethyl benzene	15.0	5.2	3.3
Phenol	<0.5	8.5	0.9
2,4-Dimethylphenol	1.6	<0.5	1.3
1,2-Dichlorobenzene	<0.5	0.5	<0.5
1,4-Dichlorobenzene	<0.5	0.6	0.5
Nitrobenzene	<0.5	2.2	10.7
Naphthalene	1.0	4.6	1.0
Acenaphthylene	<0.5	<0.5	0.6
Fluorene	<0.5	0.8	<0.5
Diethyl phthalate	0.8	2.7	2.3
N-Nitroso-diphenylamine	<0.5	<0.5	0.5
Phenanthrene	0.8	1.0	0.7
Fluoranthene	0.5	0.5	<0.5
Butylbenzyl phthalate	<0.5	0.6	<0.5
Bis(2-ethylhexyl) phthalate	0.5	0.7	0.7

No. and type of samples were not specified

Concentrations of priority pollutants in raw wastewaters samples in the EPA "40 POTW Study" (EPA , 1982a) are reported in Table 16. Generally, mean (arithmetic) concentrations were significantly higher than median concentrations which indicate that a number of high concentrations skew the data distributions. Inorganics present in high concentrations (based on median concentrations) included cyanide, zinc, copper and chromium. In the organic contaminants, compounds with the highest concentrations included methylene chloride, 1,1,1-trichloroethane, trichloroethylene, toluene, tetrachloroethylene and bis(2-ethylhexyl) phthalate. With the exception of the phthalate, the organics are all in the purgeable class.

The frequency of occurrence of contaminants in this study is also of interest because some toxics may be detected regularly at a low concentration in wastewater samples. The frequency of occurrence data for priority pollutants in the EPA 40 plant study are summarized in Table 17. Some inorganic contaminants (i.e. zinc, copper and cyanide) were observed at detectable levels in all influent samples collected. Other contaminants in this study which were found in 90 percent or more of the samples included toluene, chromium, tetrachloroethylene, methylene chloride, bis (2-ethylhexyl) phthalate, chloroform and trichloroethylene. Altogether, 23 trace contaminants were detected in more than 50 percent of the influent samples. A total of 29 organic contaminants were detected in one percent or less of the influent samples collected.

TABLE 16. SUMMARY OF SELECTED INFLUENT POLLUTANT CONCENTRATIONS IN 40 POTW STUDY (EPA, 1982a)

PARAMETER[1]	MEAN OF PLANT AVERAGE CONCENTRATIONS	MEDIAN OF PLANT AVERAGE CONCENTRATIONS
BOD (mg/L)	214	215
TSS (mg/L)	182	153
Cadmium	38	3
Chromium	173	105
Copper	226	132
Cyanide	577	249
Lead	101	53
Mercury (ng/L)	551	517
Nickel	120	54
Silver	9	8
Zinc	723	273
Benzene	20	2
1,1,1-Trichloroethane	220	29
Chloroform	17	7
1,2-trans-Dichloroethylene	7	2
Ethylbenzene	22	8
Methylene Chloride	508	38
Tetrachloroethylene	125	23
Toluene	216	27
Trichloroethylene	76	28
Phenol	54	7
Naphthalene	7	3
Bis (2-ethylhexyl) Phthalate	45	27
Butyl Benzyl Phthalate	12	3
Di-N-Butyl Phthalate	9	4
Diethyl Phthalate	4	3

1. All units in ug/L unless otherwise noted.

TABLE 17. OCCURRENCE OF PRIORITY POLLUTANTS IN INFLUENTS DURING 40 POTW STUDY (EPA, 1982a)

PARAMETERS	NUMBER OF SAMPLES ANALYZED	NUMBER OF TIMES DETECTED	PERCENT OF SAMPLES WHERE DETECTED	PARAMETERS	NUMBER OF SAMPLES ANALYZED	NUMBER OF TIMES DETECTED	PERCENT OF SAMPLES WHERE DETECTED
Zinc	282	282	100	1,3-Dichlorobenzene	287	19	7
Cyanide	284	283	100	1,1,2,2-Tetrachloroethane	288	19	7
Copper	282	281	100	Vinyl chloride	288	17	6
Toluene	288	276	96	Heptachlor	288	15	5
Chromium	282	268	95	PCB-1242	288	13	5
Tetrachloroethylene	288	273	95	2,4,6-Trichlorophenol	288	13	5
Methylene chloride	288	266	92	Fluorene	287	11	4
Bis(2-Ethylhexyl) phthalate	287	265	92	Methyl bromide	288	10	3
Chloroform	288	263	91	Beryllium	282	9	3
Trichloroethylene	288	260	90	Acenaphthene	287	9	3
1,1,1-Trichloroethane	288	244	85	Chrysene	287	9	3
Ethylbenzene	288	231	80	1,2-Benzanthracene	287	9	3
Nickel	282	224	79	Delta-BHC	288	9	3
Phenol	288	228	79	Parachlorometa cresol	288	9	3
Silver	282	200	71	2-Chlorophenol	288	9	3
Mercury	282	196	70	Thallium	282	8	3
Di-N-Butyl phthalate	287	185	64	Chlorodibromomethane	288	8	3
Lead	282	176	62	Bromoform	288	7	2
1,2-trans-Dichloroethylene	288	179	62	Dichlorodifluoromethane	288	7	2
Benzene	288	175	61	1,3-Dichloropropylene	288	7	2
Butylbenzyl phthalate	287	165	57	Isophorone	287	5	2
Cadmium	282	157	56	N-Nitrosodiphenylamine	287	5	2
Diethyl phthalate	287	151	53	Hexachlorobenzene	287	4	1
Naphthalene	287	142	49	1,2-Diphenylhydrazine	287	4	1
1,1-Dichloroethane	288	89	31	Aldrin	289	4	1
Pentachlorophenol	287	84	29	Indeno(1,2,3,-c,d)pyrene	280	3	1
gamma-BHC	288	75	26	Benzo(a)pyrene	284	3	1

TABLE 17. OCCURRENCE OF PRIORITY POLLUTANTS IN INFLUENTS DURING 40 POTW STUDY (EPA, 1982a) (cont'd)

PARAMETERS	NUMBER OF SAMPLES ANALYZED	NUMBER OF TIMES DETECTED	PERCENT OF SAMPLES WHERE DETECTED	PARAMETERS	NUMBER OF SAMPLES ANALYZED	NUMBER OF TIMES DETECTED	PERCENT OF SAMPLES WHERE DETECTED
1,1-Dichloroethylene	288	74	26	2,4-Dinitrotoluene	287	3	1
1,2-Dichlorobenzene	287	67	23	alpha-Endosulfan	288	3	1
Phenanthrene	287	57	20	Chloroethane	288	3	1
Anthracene	287	52	18	PCB-1254	288	3	1
1,4-Dichlorobenzene	287	49	17	Bis(2-Chloroethyoxy)methane	276	2	1
Arsenic	282	43	15	Benzo(a)perylene	280	2	1
1,2-Dichloroethane	288	42	15	Dibenz(a,h)anthracene	280	2	1
Antimony	282	39	14	Benzo(b)fluoranthene	285	2	1
Chlorobenzene	288	36	13	Benzo(a)fluoranthene	286	2	1
Dimethyl phthalate	287	33	11	Hexachloroethane	287	2	1
Methyl chloride	288	33	11	2-Chloronaphthalene	287	2	1
1,2,4-Trichlorobenzene	287	28	10	4,4'-DDD	287	2	1
2,4-Dimethylphenol	288	28	10	beta-BHC	288	2	1
Carbon-Tetrachloride	288	25	9	Dieldrin	288	2	1
Trichlorofluoromethane	288	25	9	Heptachlor Epoxide	288	2	1
Selenium	282	24	9	Acenaphythylene	287	1	LT 1
Dichlorobromomethane	288	24	8	Hexachlorobutadiene	287	1	LT 1
Alpha-BHC	288	22	8	2,6-Dinitrotoluene	287	1	LT 1
1,1,2-Trichloroethane	288	21	7	4-Bromophenyl phenyl ether	287	1	LT 1
1,2-Dichloropropane	288	21	7	Acrylonitrile	287	1	LT 1
Di-N-Octyl phthalate	287	20	7	2-Chloroethyl vinyl ether	288	1	LT 1
Fluoranthene	287	20	7	2-Nitrophenol	288	1	LT 1
2,4-Dichlorophenol	288	20	7	2,4-Dinitrophenol	288	1	LT 1
Pyrene	287	19	7	4,4'-DDT	288	1	LT 1

* Pollutants not listed were never detected.
* Occurrences are based on all influent samples taken.
* Pollutants reported as less than the detection limit and unconfirmed pesticides are assumed not detected.

TRACE CONTAMINANT CHARACTERIZATION DATA

In addition to the "priority pollutants" in raw wastewater, which are now being monitored on a semi-regular basis (i.e. from once per year to once per month) in the U.S. as a result of state "pretreatment" programs, other organic contaminants are found in significant quantities. An estimate of the total loadings of organic contaminants in wastewater treatment plant influents was prepared for a Report to Congress by the U.S. EPA (1986). Of the contaminants listed, eight of the first twenty organics ranked by loading were non-priority pollutants, and included xylenes, methyl ethyl ketone, acetone, ethyl acetate, methanol, trichlorotrifluoroethane, butanol and methyl isobutyl ketone. The relative loadings to the treatment plants are reported in Table 18.

TABLE 18. RELATIVE LOADINGS OF ORGANIC COMPOUNDS IN U.S. TREATMENT PLANTS (FROM EPA, 1986)

ORGANIC CONSTITUENT	FREQUENCY OF DETECTION, 40 POTW STUDY (%)	U.S. NATIONAL INFLUENT AVERAGE LOADING (tonne/yr)
Methylene chloride	92	7,937
Toluene	96	3,232
Tetrachloroethylene	95	2,569
1,1,1-Trichloroethane	85	2,503
Trichloroethylene	90	2,224
Bis(2-ethylhexyl) phthalate	92	1,713
Xylenes	--	1,678
Methyl ethyl ketone	--	1,435
Phenols, phenolic resins	79	1,238
Ethyl benzene	80	963
Acetone	--	920
Ethyl acetate	--	648
Chloroform	91	515
Methanol	--	470
Dichlorodifluoroethane	2	412
Trichlorotrifluoroethane	--	389
Butanol	--	380
Methyl isobutyl ketone	--	386
Benzene	61	354
Butylbenzyl phthalate	57	345
1,2-Dichlorobenzene	23	320
Chloromethane	11	316
Dibutyl phthalate	64	299
Naphthalene	49	295
Carbon tetrachloride	9	278
Cresol	--	240
Chlorobenzene	13	136
Diethyl phthalate	53	122
Isobutanol	--	113
Formaldehyde	--	107
1,4-Dichlorobenzene	17	70
Trichlorofluoroethane	9	52
Dimethyl phthalate	11	33
Diethyl ether	--	23
Aniline	--	19
Pyridine	--	2
Dichloropropane	7	2
Vinyl chloride	6	1

TRACE CONTAMINANT CHARACTERIZATION DATA

A longer term study of 30 day duration was also carried out for the U.S. EPA at the Moccasin Bend treatment plant in Chattanooga, Tennessee (EPA, 1982b). A six day study also took place at this plant just prior to the longer study. Arithmetic mean concentrations for these two study periods are summarized in Table 19. Organics present in the highest concentrations were toluene, phenol, methylene chloride, chloroform and tetrachloroethylene, whereas metals with the highest observed levels were zinc, chromium, cyanide, copper and nickel.

In the EPA 30 day study, seven toxics (chromium, copper, silver, zinc, benzene, methylene chloride and tetrachloroethylene) were observed in 100 percent of the influent wastewater samples collected (Table 19). Five additional contaminants were found at detectable levels on all but one day during the 30 day sampling period, and included cyanide, chloroform, toluene, trichloroethylene, and phenol. Base/neutral and acid extractable compounds (other than phenol) were observed less frequently than the inorganics and purgeables.

TABLE 19. MEAN CONCENTRATIONS AND VARIABILITY OF PRIORITY POLLUTANTS IN INFLUENT SAMPLES DURING EPA 30 DAY STUDY (FROM EPA, 1982b)

PARAMETER[1]	30-DAY STUDY			SIX-DAY STUDY		
	% OCCURRENCE	MEAN (ug/L)	STANDARD DEVIATION (ug/L)	% OCCURRENCE	MEAN (ug/L)	STANDARD DEVIATION (ug/L)
Volatiles						
Benzene	100	18	12	100	14	8
1,1,1-Trichloroethane	83	20	49	100	43	49
Chloroform	97	73	36	100	77	59
Ethylbenzene[2]	86	23	18	100	20	17
Methylene chloride[2]	100	88	86	100	40	30
Toluene[2]	97	321	325	100	378	236
Trichloroethylene	97	26	51	100	10	12
Tetrachloroethylene	100	52	87	100	81	52
Acids						
Phenol	97	201	155	100	448	209
2,4-Dichlorophenol	72	5	7	83	2	2
Base/Neutrals						
1,2,4-Trichlorobenzene	79	17	22	100	100	45
1,3-Dichlorobenzene	79	2	6	17	1	1
1,4-Dichlorobenzene	48	5	8	100	4	3
Naphthalene	66	11	11	100	55	45
Bis(2-ethylhexyl) phthalate	79	12	15	100	14	7
Di-n-Butyl phthalate	52	5	14	100	4	2
Diethyl phthalate	48	4	8	100	6	3
Metals						
Chromium	100	225	527	100	226	160
Copper	100	77	25	100	123	24
Cyanide	97	83	84	100	4747	1664
Mercury (ng/L)	66	303	270	17	333	816
Nickel	72	73	76	100	98	37
Silver	100	5	2	100	21	7
Zinc	100	332	164	100	486	132
Conventional						
BOD_5	—	303	115	—	435	112
TSS	--	232	93	--	327	95

1. Influent variability analysis conducted on priority toxic pollutants detected 50 percent of the time or greater for combined 36-day period.

2. Outlier values were removed from database.

TRACE CONTAMINANT CHARACTERIZATION DATA

The influent wastewater at four U.S. treatment plants was characterized by A.D. Little (1979) in a study aimed at determining the sources of toxics in POTWs. In the four plants examined (Cincinnati, St. Louis, Atlanta, Hartford), organic contaminants present in the highest concentrations were tetrachloroethylene, trichloroethylene, naphthalene, 1,1,1-trichloroethane, toluene and butyl benzyl phthalate. Zinc, chromium, lead and copper were the inorganics present in highest concentrations. The mean concentrations and frequency of occurrence of pollutants in this study are reported in Table 20. Copper, zinc and chloroform were detected in 100 percent of all samples (i.e. in all samples from each of the four cities).

TABLE 20. SUMMARY OF RAW WASTEWATER CONTAMINANT CONCENTRATIONS IN FOUR TREATMENT PLANTS (A.D. LITTLE, 1979)

CONTAMINANT	TREATMENT PLANT								TOTAL % OCC.	MEAN CONC'N (ug/L)
	CINCINNATI		ST. LOUIS		ATLANTA		HARTFORD			
	n	$\bar{x}$ (ug/L)	n	$\bar{x}$ (ug/L)	n	$\bar{x}$ (ug/L)	n	$\bar{x}$ (ug/L)		
1,1-Dichloroethylene	0	0	1	0.9	2	8.6	0	0	17	2.4
1,1-Dichlorothane	0	0	1	0.3	0	0	0	0	6	0.1
1,2-t-Dichloroethylene	0	0	2	0.5	3	18.6	0	0	28	4.8
Chloroform	6	2.6	6	6.2	3	7.1	3	3.6	100	4.9
1,2-Dichloroethane	1	0.4	0	0	1	0.4	0	0	11	0.2
1,1,1-Trichloroethane	2	0.3	6	9.3	3	95.9	3	10.3	78	28.9
Bromodichloromethane	0	0	2	0.7	0	0	0	0	11	0.2
Trichloroethylene	0	0	6	28.6	3	164.9	3	8.4	67	50.5
Benzene	6	3.7	6	7.0	0	0	0	0	67	2.7
Chlorodibromomethane	0	0	4	1.0	0	0	0	0	22	0.2
Tetrachloroethylene	3	1.1	6	45.0	3	239.4	3	26.2	83	77.9
Toluene	2	1.9	6	60.2	3	25.5	3	15.6	78	25.8
Chlorobenzene	0	0	1	0.2	0	0	0	0	6	0
Ethyl benzene	3	0.9	6	15.6	3	48.7	0	0	67	16.3
Phenol	0	0	4	10.5	2	18.8	0	0	33	7.3
2,4-Dimethylphenol	0	0	0	0	2	9.9	0	0	11	2.5
Pentachlorophenol	1	3.8	0	0	3	19.2	0	0	22	5.7
Naphthalene	2	0	4	26.1	2	92.7	0	13.4	44	33.1
Diethyl phthalate	4	11.6	3	7.0	1	5.0	1	3.6	50	6.8
Di-n-butyl phthalate	4	12.6	6	15.8	1	4.4	1	4.2	67	9.3
Butylbenzyl phthalate	0	0	5	11.4	3	77.3	0	0	44	22.2
Bis(2-Ethylhexyl) phthalate	2	4.5	2	4.3	0	0	0	0	22	2.2
Arsenic	6	21.6	0	0	0	0	2	1.9	44	5.9
Cadmium	4	2.4	4	2.9	2	3.1	0	0	56	2.1
Chromium	4	151.6	6	135.4	3	72.1	3	65.4	89	106.1
Copper	6	62.1	6	46.6	3	50.4	3	96.6	100	63.9
Lead	4	15.9	6	210.2	3	135.6	3	35.6	89	99.3
Mercury	1	0.4	1	0.5	1	0.8	0	0	17	0.4
Nickel	3	34.8	6	45.8	3	18.3	3	35.0	83	33.5
Zinc	6	372.0	6	290.6	3	353.2	3	157.4	100	293.3
Cyanide	4	39.7	8	14.6	1	4.9	1	4.0	61	15.8

n = No. of Detections

No. of grab samples analyzed = 6 for Cincinnati & St. Louis
= 3 for Atlanta & Hartford

TRACE CONTAMINANT CHARACTERIZATION DATA

In a report to the U.S. Congress on hazardous wastes entering POTWs, the EPA (1986) reported contaminant levels in the raw wastewater of two plants. The results of the limited survey are reported in Table 21. In general, Plant #1001 had more contaminants at higher concentrations than Plant #1002. Zinc, copper, chromium, acetone and methyl ethyl ketone were the principal contaminants at the former plant. Only zinc and acetone were present in the same concentration range at Plant #1002.

TABLE 21. RAW WASTEWATER CONTAMINANT CONCENTRATION AT 2 POTWs (EPA, 1986)

CONTAMINANT	CONCENTRATION (ug/L)	
	PLANT #1001	PLANT #1002
Cadmium	5	7
Chromium	117	51
Copper	485	<25
Mercury	0.2	0.5
Lead	28	<5
Zinc	1,030	150
Acetone	182	106
Methyl ethyl ketone	135	<50
Methylene chloride	12	28
Phenol	11	<11
Tetrachloroethylene	24	<10
Toluene	22	<10
1,1,1-Trichloroethane	59	<10
alpha-BHC	0.033	<0.003
4,4'-DDE	0.0166	<0.004
Captofol	0.832	<0.010
Endrin ketone	0.0249	<0.010
Fluchloralin	2.66	<0.010
Mirex	0.249	<0.010
Pronamide	<0.010	0.07
Trifluralin	1.50	<0.010

No. and type of samples not specified

Concentrations and removals of toxic contaminants at the Hamilton, Ontario WPCP were studied by CANVIRO Consultants Ltd. (1984a). The study focussed on polynuclear aromatic hydrocarbons (PAHs), trace metals and selected contaminants in the PCB/pesticide group. Influent concentrations are summarized in Table 22. Most trace metal concentrations, especially zinc, were present in higher concentration than either the PAHs or PCB/pesticide group.

In United Kingdom wastewater samples, mean concentrations of the PCB Aroclor 1260, 4,4-DDE and Dieldrin were 0.059, 0.024 and 0.031 ug/L, respectively (McIntyre et al, 1981). The RSD of the means was surprisingly small, ranging from 18 percent of the mean for 4,4-DDE and Dieldrin, to 24 percent for Aroclor 1260.

TABLE 22. MEAN CONCENTRATIONS OF SELECTED CONTAMINANTS IN HAMILTON, ONTARIO RAW WASTEWATER (CANVIRO Consultants Ltd., 1984a)

ORGANIC CONTAMINANT	MEAN CONCENTRATION (ug/L)	INORGANIC CONTAMINANT	MEAN CONCENTRATION (ug/L)
Naphthalene	13.4	Arsenic	2
Acenaphthalene	5.8	Cadmium	1
Dibenzofuran	10.9	Chromium	210
Fluorene	14.5	Copper	130
Fluoranthene	38.7	Mercury	0.26
Carbazole	21.6	Nickel	90
Pyrene	35.3	Lead	90
Benzo(a)pyrene	41.1	Zinc	3,300
Lindane	0.09		
Total PCBs	0.13		
Pentachlorophenol	0.23		

No. of 24-hr composite samples = 28

Hourly variation in the flow and trace metal concentrations in wastewater collected at the outlet of the right side bar screen at the Edmonton Gold Bar WPCP are illustrated in Figure 1 (Neilsen and Hrudey, 1983). It is clear that the plant was subject to periodic spikes of chromium and zinc over the four day study period. Geometric mean concentrations of metals in the raw wastewater are reported in Table 23. Geometric means were calculated by Neilsen and Hrudey because cumulative frequency plots indicated that, with the exception of chromium with the transient spike levels, the other metals concentration were distributed in a log normal manner.

TABLE 23. INFLUENT METAL CONCENTRATIONS TO EDMONTON GOLD BAR WPCP (NEILSEN AND HRUDEY, 1983)

	TRACE METALS				
	Cd	Cr	Cu	Ni	Zn
Range (ug/L)	0.8-9.2	95-4,500	39-295	15-300	80-840
Geometric Mean (ug/L)	2.6	254	90	42	190

No. of grab samples = 96

Influent concentrations for some organic contaminants in New York City wastewater are reported in Table 24 (Iannone et al, 1984). On a flow-weighted basis, methylene chloride and total phenols are found in the highest concentrations, 279 and 250 ug/L, respectively. Occurrence data for some of these contaminants are also provided. The most frequently occurring organics were methylene chloride, tetrachloroethylene and phenol.

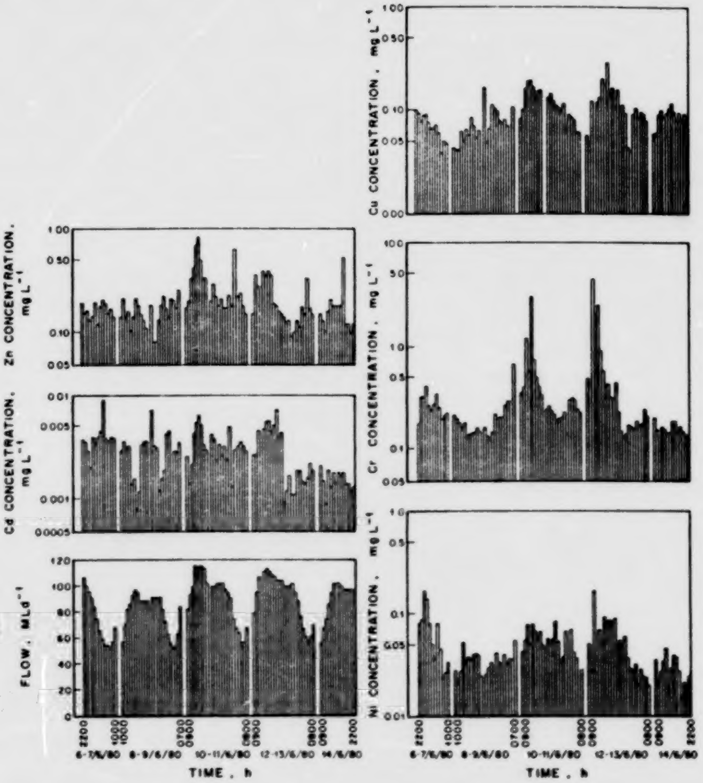

FIGURE 1— HOURLY FLUCTUATIONS OF RAW WASTEWATER TRACE METALS AND FLOW AT EDMONTON, ALBERTA WASTEWATER TREATMENT PLANT (NEILSEN AND HRUDEY, 1983)

TABLE 24. FLOW-WEIGHTED CONCENTRATIONS OF ORGANIC CONTAMINANTS IN NEW YORK CITY WASTEWATERS (IANNONE ET AL, 1984)

ORGANIC CONTAMINANT	INFLUENT CONCENTRATION (ug/L)	INFLUENT OCCURRENCE (%)
Methylene chloride	279	83
Total phenols	250	56
1,1,1-trichloroethane	48	
Bis(2-ethylhexyl) phthalate	31	39
Tetrachloroethylene	23	65
Phenol	22	
Toluene	14	31
Trichloroethylene	12	
Methyl chloride	8	

No. and type of samples not specified

In a Puerto Rican raw wastewater, zinc was significantly higher in concentration than any of the other metals, at 1,830 ug/L (Roman-Seda, 1984). Phenol was relatively high at a mean concentration of 865 ug/L. The relative standard deviation of the mean ranged from 42 to 66 percent for the metals, and 26 percent for phenol. The Puerto Rican data are summarized in Table 25.

TABLE 25. REPORTED LEVELS OF SELECTED CONTAMINANTS IN A PUERTO RICAN TREATMENT PLANT INFLUENT (ROMAN-SEDA, 1984)

CONTAMINANT	MEAN CONCENTRATION (ug/L)	RELATIVE STANDARD DEVIATION (%)
Phenol	865	26
Copper	130	46
Chromium (VI)	190	42
Lead	80	50
Zinc	1830	66

No. of 24-hr composite samples = 33

Summary of Raw Wastewater Data

From reviewing contaminant concentration and occurrence data in raw municipal wastewater, it can be concluded that there is no "typical" composition of contaminants. Some wastewaters have numerous organic compounds identified as present (e.g. Racine, Wisconsin; Cleveland Westerly and Southerly) whereas other plants have few detectable compounds (e.g. Lima, Ohio; Madison, Wisconsin). Although certain metals tend to be present in most wastewaters at detectable levels, the concentrations can vary widely from one plant to another as illustrated by the data from Indiana municipalities.

Factors that may contribute to contaminant variability between treatment plants due to different types of industries, degree of pretreatment required by municipality or other authority, type and frequency of samples collected, and analytical methods used. Wastewater contaminant variability is discussed in greater detail in Section 5.1.

In spite of substantial between-plant variability of contaminant concentrations, a number of general trends are apparent. The most frequently identified contaminants include the inorganics (metals and cyanide), purgeables, phthalate esters, naphthalene and phenol. Metals are typically present in the highest concentrations (e.g. 100 to 1,000 ug/L), while organics tend to be observed, when present, at low concentrations, on the order of 1 to 100 ug/L. Specific contaminants, both organic and inorganic, may be substantially higher in concentration at site-specific locations. Generally speaking, trace organic concentrations in Canadian raw wastewaters appeared to be lower than in American treatment plant influents, while trace metals concentrations are similar in magnitude in Canadian and American raw wastewaters.

3.2 Trace Contaminants in Industrial Wastewaters

Because industry requires such a wide range of chemicals for manufacturing or provision of services, the range of contaminants is bound to be extensive overall and yet somewhat industry specific. Characterization of the industrial discharges is clearly a formidable task. Two major efforts by the U.S. Environmental Protection Agency have attempted to characterize the wastewaters of numerous industrial sectors. The "Treatability Manual", first published by the EPA in 1980, was prepared from numerous Development Documents, which were drafted to provide effluent limitation guidelines for Best Available Technology (BAT) and Best Practical Technology (BPT) for industrial pretreatment programs in the U.S. The Treatability Manual summarizes data with respect to contaminants in industrial wastewaters, treatment technologies for removal of contaminants, and costing of the treatment technologies. This manual has been updated in 1982 and 1983 to include new data generated since the original manual was published. Industrial sectors with wastewaters characterized by this manual are noted in Table 26. The Treatability Manual contains a very large amount of data on contaminant levels in various industrial wastewaters. Because it is not useful to reproduce the data in this report, for characterization data, the reader is referred to the Treatability Manual (EPA, 1983).

Additional characterization data were provided in a Report to the U.S. Congress by the EPA for assessment of impact of hazardous wastes discharged to Publicly Owned Treatment Works (POTWs) (EPA, 1986). The industrial characterization data is compiled mainly in Appendix I of the EPA report, to which the reader is referred for actual contaminant levels. Industrial sectors addressed by this report are also summarized in Table 26.

One limitation to these data is the small number of industries within certain sectors used for characterization, and the inclusion of only EPA priority pollutants in the Treatability Manual (EPA, 1980). These reports are however, the most comprehensive sources of industrial wastewater characterization data available in the published literature.

The occurrence and concentration of contaminants in industrial wastewaters are typically industry specific. For example, in the EPA (1986) Report to Congress, wastewater from a solvent recovery facility had almost no metals, but high concentrations of acetone and benzene as shown in Table 27. The wastewater from a paint manufacturing plant contained elevated levels of chromium and zinc and particularly high levels of the

TRACE CONTAMINANT CHARACTERIZATION DATA

TABLE 26. INDUSTRIAL SECTOR WITH DATA CHARACTERIZING WASTEWATER DISCHARGES

INDUSTRIAL SECTOR	TREAT-ABILITY MANUAL (EPA, 1980)	REPORT TO CONGRESS (EPA, 1986)	SIC GROUP (Scott's Directory, 1987)
Adhesives & Sealants		X	2891
Battery Manufacturing	X	X	3691,3692
Coal Mining	X		1111,1112, 1211,1213
Coal & Petroleum Refining	X	X	2911
Coil Coating	X		3479
Cosmetics, Fragrances, Flavours & Food Additives		X	2844,2087
Electrical & Electronics Components	X	X	Group 36
Equipment Manufacturing & Assembly		X	Group 35
Electrical Power Generation	X	X	4911,4931
Electroplating & Metal Finishing	X	X	3471
Explosives	X		2892
Fertilizer Manufacturing		X	2873,2874
Food & Food By-products		X	Group 20
Foundries	X		3321,3322, 3324,3361, 3362,3369
Gum & Wood Chemicals	X	X	2861
Hazardous Waste Site Cleanup		X	
Industrial & Commercial Laundries	X	X	Group 7210
Ink Manufacturing & Formulation	X	X	2893
Inorganic Chemical Manufacturing	X	X	Group 2810
Iron & Steel Manufacturing	X	X	Group 3310
Laboratories & Hospitals		X	
Leather Tanning & Finishing	X	X	3111
Miscellaneous Chemical Formulation		X	2899
Motor Vehicle Services		X	
Non-Ferrous Metal Forming or Manufacturing	X	X	Group 3330
Organic Chemicals Plastics & Synthetic Fibers Manufacturing	X	X	Group 2820
Paint Manufacturing & Formulation	X	X	2851
Pesticides Manufacturing & Formulation		X	2879
Pharmaceutical Manufacturing	X	X	2834
Photographic Chemicals & Supplies	X	X	3861
Plastics Molding & Forming		X	3079
Porcelain Enamelling	X	X	3469
Printing & Publishing		X	
Pulp and Paper Mills	X	X	2611,2621
Rubber Manufacturing & Processing	X	X	3069
Service Related Industries		X	
Soaps & Detergents Manufacturing	X	X	2841
Stone & Mineral Products	X	X	Group 32
Textile Mills	X	X	Groups 22,23
Timber Products Processing	X	X	Group 24
Transport Services		X	
Waste Reclamation Services		X	
Waste Treatment & Disposal Services	X	X	
Wholesale Trade Industry		X	
Wood Furniture Manufacturing & Refinishing		X	Group 25

TABLE 27. CONCENTRATION OF CONTAMINANTS IN SELECTED INDUSTRIAL WASTEWATERS (EPA, 1986)

CONTAMINANT	CONCENTRATION (ug/L)			
	PHARMACEUTICAL INDUSTRY	PAINT INDUSTRY	SOLVENT RECOVERY	INDUSTRIAL LAUNDRY
Antimony	15	<10		121
Arsenic	8	58		5
Cadmium	8	30	8	25
Chromium	99	4,620		261
Copper	45	58		487
Mercury	0.4	ND	6.1	0.8
Nickel	ND	ND		106
Lead	13	122		400
Zinc	303	3,390	35	1,960
Acetone	4,592	4,576	415,000	1,542
Benzene	17		26,130	
Biphenyl			85	
Bis(2-ethylhexyl) phthalate		<1,000		1,192
Chlorobenzene	19			
Chloroform	50			10
Diethyl ether	287			
Diphenyl ether			223	
Ethylbenzene	136	2,183		177
Isophorone				690
Methylene chloride	2,760	481,600	5,319	
Naphthalene			15	40
Methyl ethyl ketone	1,566	119,700		427
Phenol		1,818	129	
Styrene		2,329		
Tetrachloroethylene	43			213
Toluene	1,565	621	438	548
Trans-1,2-dichloroethylene	442			
Trichloroethylene	87		352	15
Vinyl chloride	42			
1,1-Dichloroethane	76			
1,1-Dichloroethylene	22			
1,1,1-Trichloroethane	393			478
1,1,2-Trichloroethane			2,090	
1,1,2,2-Tetrachloroethane			2,090	
1,2-Dichloroethane	2,497			
1,2-Dichlorobenzene	2,280			
n-Decane				394
n-Dodecane				180
n-Tetradecane				85
n-Hexadecane				162
n-Octadecane				115
n-Eicosane				159

solvents methylene chloride and methyl ethyl ketone. Pharmaceutical industry wastewater was found to have low concentrations of metals but high levels of solvents such as acetone, methylene chloride, methyl ethyl ketone, 1,2-dichloroethane and 1,2-dichlorobenzene. The wastewater discharged by an industrial laundry contained elevated levels of zinc, acetone and bis(2-ethylhexyl) phthalate, as well as longer-chain alkanes (C_{10}-C_{20}) in the 100 to 400 ug/L concentration range. The alkanes were not observed in other industrial wastewaters in this EPA (1986) survey.

Wastewaters from five organic chemicals manufacturing plants were characterized in a study sponsored by the U.S. Chemical Manufacturers Association (CMA) and the Environmental Protection Agency (EPA). The data were presented as a pooled database of the 5 chemical plant wastewaters. The geometric mean concentrations of priority pollutants identified in five organic chemical wastewaters are reported in Table 28. Contaminants present in the highest concentrations in wastewaters discharged to pretreatment systems were acrylonitrile, toluene, nitrobenzene, bromomethane, and naphthalene (Engineering Science Inc., 1982). The most frequently detected organics were benzene, toluene, ethyl benzene and 2,4,6-trichlorophenol. Compounds displaying the greatest variability in the industrial wastewater samples were chloroform, di-n-butyl phthalate, bis(2-ethylhexyl) phthalate, 1,1-dichloroethylene and carbon tetrachloride. As noted above, interpretation of the variability data is difficult because it includes both within-plant and between-plant variations.

Nutt and Marvan (1984) identified many EPA priority pollutants and other trace contaminants in coke plant wastewaters. The concentrations of several compounds exceeded 1,000 ug/L, including phenol, 2,4-dimethyphenol, quinoline, isoquinoline, indole, carbazole and several methyl-substituted quinolines. A number of PAHs were identified at concentrations ranging from 3 to 333 ug/L. Concentrations are summarized in Table 29.

In the A.D. Little Co. (1979) study of contributors to POTW influents, two catchment areas were identified as being predominantly industrial. The occurrence and mean concentrations of priority pollutants in these two locations are reported in Table 30. Chloroform, trichloroethylene, tetrachloroethylene, toluene, chromium, copper, lead, nickel and zinc were detected in all samples collected. The metals were typically present in concentrations ranging from 100 to 900 ug/L, while the organics were generally in the range 10 to 100 ug/L. Certain contaminants were site specific: bromodichloromethane and dibromochloromethane were found in all St. Louis samples, but not in Atlanta samples. Conversely, the organics 1,1-dichloroethylene, 2,4-dimethylphenol, pentachlorophenol and bis(2-ethylhexyl) phthalate were frequently observed in Atlanta industrial wastewater but not St. Louis wastewater. Variability of the contaminants at the sites investigated was not reported.

In many cases, pretreatment of industrial wastewaters is required to reduce contaminants to concentrations acceptable for discharge to municipal sewers or receiving waters. The impact of trace contaminants from industry on POTW discharges is then reduced. Concentrations of trace contaminants in industrial wastewaters prior to biological treatment are summarized in Table 31 (Myers et al, 1979). Industrial sectors examined included (1) organics and plastics, (2) pharmaceuticals, (3) pesticides, (4) rubber, (5) wood preserving and (6) petroleum

TRACE CONTAMINANT CHARACTERIZATION DATA

TABLE 28. CHARACTERIZATION OF CONTAMINANTS IN ORGANIC CHEMICAL WASTEWATER TREATMENT SYSTEMS (ENGINEERING-SCIENCE, 1982)

COMPOUND	INFLUENT		
	GEOMETRIC MEAN (ppb)	STANDARD DEVIATION ($\log_e$ scale)	NUMBER OF DETECTIONS
Purgeables			
Acrylonitrile	10,300	1.902	47
Benzene	581	1.963	129
Bromomethane	1,250	1.396	9
Bromodichloromethane	20	1.251	29
Carbon tetrachloride	51	2.025	3
Chlorobenzene	20	1.086	29
Chloroethane	12	1.755	19
Chloroform	348	2.230	63
Dibromochloromethane	6	0.475	22
1,1-Dichloroethane	9	1.398	22
1,2-Dichloroethane	524	1.252	73
1,1-Dichloroethene	42	2.064	53
t-1,2-Dichloroethene	42	1.931	7
1,2-Dichloropropane	138	1.133	54
1,2-Dichloropropene	148	1.199	47
Ethyl benzene	283	1.640	107
Methylene chloride	17	1.529	61
1,1,2,2-Tetrachloroethane	17	1.733	2
Tetrachloroethene	6	0.521	31
1,1,1-Trichloroethane	7	0.543	38
1,1,2-Trichloroethane	12	0.876	15
Trichloroethene	7	0.586	31
Trichlorofluoromethane	ND	--	0
Toluene	4,500	0.809	112
Vinyl chloride	6	0.438	4
All Purgeable Pollutants	166	2.655	1,007
Acid Extractables			
4-Chloro-3-methylphenol	ND	--	0
2-Chlorophenol	53	1.183	57
2,4-Dichlorophenol	347	0.765	43
2,4-Dimethylphenol	270	1.992	12
2,4-Dinitrophenol	673	1.247	44
2-Nitrophenol	40	0.628	38
Pentachlorophenol	216	1.330	49
Phenol	171	1.820	137
2,4,6-Trichlorophenol	100	1.210	89
All Acid Pollutants	150	1.586	469

TABLE 28. CHARACTERIZATION OF CONTAMINANTS IN ORGANIC CHEMICAL WASTEWATER TREATMENT SYSTEMS (ENGINEERING-SCIENCE, 1982) (cont'd)

COMPOUND	INFLUENT		
	GEOMETRIC MEAN (ppb)	STANDARD DEVIATION ($\log_e$ scale)	NUMBER OF DETECTIONS
Base/Neutral Extractables			
Acenaphthene	84	0.611	9
Acenaphthylene**	65	0.514	10
Anthracene[1]/Pnenanthrene[1]	62	1.655	14
Benzo(a)anthracene[2]/ Chrysene[2]	20	1.027	10
Benzo(b)fluoranthene[1]/ Benzo(k)fluoranthene[3]	11	0.979	10
Benzo(a)pyrene	13	0.953	11
Bis(2-ethylhexyl) phthalate	24	2.070	47
Butylbenzyl phthalate**	12	1.529	5
Chrysene	ND	--	0
Dibenzo(a,h)anthracene	15	--	1
Di-n-butyl phthalate	86	2.098	44
1,3-Dichlorobenzene*/ 1,4-dichlorobenzene	5	--	1
1,2-Dichlorobenzene	331	1.354	43
Diethyl phthalate**	134	1.964	36
Dimethyl phthalate	46	2.011	31
Dioctyl phthalate	28	1.117	6
Fluoranthene	17	1.347	19
Fluorene	56	0.693	10
Isophorone	650	--	1
Napthalene	802	1.930	11
Nitrobenzene	3,000	2.010	32
Pyrene	17	1.357	19
1,2,4-trichlorobenzene**	234	1.026	46
All Base/Neutral Pollutants	119	2.157	416

1,2,3. Reported as isomer pairs.

Note: ND = Not Detected

* All detections were less than 10 ppb

** Note: There was some question in the proper identification of these compounds in some of the samples, based on the following information:

1) 1,2,4-trichlorobenzene - most likely the co-isomer, 2,4,6-tri-benzene, which is not on the priority pollutant list.
2) Diethylphthalate - interference with dimethyl nitroaniline which co-elutes with the phthalate ester.
3) Acenaphthylene - interference with dichloroaniline or biphenyl which co-elutes with acenapthylene.
4) Butylbenzyl phthalate - most likely a product from a manufacturing process and not the phthalate ester.

TRACE CONTAMINANT CHARACTERIZATION DATA

TABLE 29. TRACE ORGANIC CONTAMINANTS IN UNTREATED COKE PLANT WASTEWATERS (NUTT AND MARVAN, 1984)

COMPOUND	CONCENTRATION* (ug/L)							
	FEED A6 (14/10/80)	FEED SS1 (1/12/80)	FEED SS1 (12/12/80)	FEED SS1 (1/04/81)	FEED SS1 (12/05/81)	FEED SS2 (1/06/81)	FEED V1 (20/10/81)	FEED V3 (24/11/81)
ACID GROUP								
p-Chloro-m-cresol					4			
2,4-Dimethylphenol				300	1098	5,840	>360	
Phenol				5,400		206,000	>100,000	
BASE NEUTRAL GROUP								
Polynuclear Aromatics:								
Acenaphthene	15	14	12	2	3	15		
Acenaphthylene	36	18	13	15	7	333	20	
Anthracene/Phenanthrene	107	87	52			227	30	
Benzo(a)anthracene/ Chrysene							>10	
Benzo(k)fluoranthene	tr	tr						
Benzo(g,h,i)perylene	tr							
Fluoranthene		45	54	10	8	43	20	
Fluorene		tr		6	4	33	10	
Indeno(1,1,2-cd)pyrene	tr							
Naphthalene	81	37	26	10	3	67	20	
Pyrene	15	3	13	5	5	49	20	
Chlorinated Benzenes:								
1,2-Dichlorobenzene	tr	16	11	tr			<10	
1,4-Dichlorobenzene or 1,3-Dichlorobenzene				tr	tr	227	50	
1,2,4-Trichlorobenzene					tr	25	<10	
Nitrosamines:								
N-nitrosodiphenylamine	16	3	2	5	3		<10	
Phthalate Esters:								
Butyl benzyl phthalate					tr			
Di-n-butylphthalate	5	17	5	13	3	173	20	
Diethylphthalate	1	1	tr	2	tr	8		
Dimethylphthalate				tr	tr	5	<10	
Di-n-octylphthalate	tr							
bis(2-ethylhexyl)phthalate	5		3	8	5			
Haloethers:								
bis(2-chloroethoxy)methane					tr	95		
bis(2-chloroethyl)ether					431	7	<10	
bis(2-chloroisopropyl)-ether	1		6					
Other Compounds:								
3,3-Dichlorobenzidine	tr		tr					
1,2-Diphenylhydrazine	50							
Isophorone					124			
3,4-Dimethylpyridine				10	12			
Isoquinoline			7,000	1,000				6,000***
2-Methylnaphthalene			16	2	111	91		20
Indole			26,000			23		9,000
2 &/or 8-methyl quinoline			2,000		84	67		1,000
"7A"-Methyl quinoline			2,000	451	66	187		560
"7B"-Methyl quinoline			691	10		2,680		150
2,6 &/or 2,7-Dimethyl quinoline			76	36	41	49		20
2,4-Dimethyl quinoline			72	41				40
3,4 &/or 5,6-Benzoquinoline			148	58	46	191		80
Carbazole			2,000	437	330	2,207		890
3,5-Dimethyl pyridine				tr	6			
Quinoline			10,000	2,000	805	7,550		17,000***
1-Methylnaphthalene						40		
4-Methyl quinoline			274	89	3	209	70	
Dibenzofuran			20	4	4	19		20
7,8-Benzoquinoline			42	13	15	113		
9-Anthracenecarbonitrile			38	tr	1			
Aniline								80

* tr <1 ug/L *** Column overload, quantitation inaccurate

TABLE 30. OCCURRENCE AND CONCENTRATION OF PRIORITY POLLUTANTS IN TWO INDUSTRIAL WASTEWATERS (A.D. LITTLE, 1979)

CONTAMINANT	ST.LOUIS % OCCURRENCE	ATLANTA % OCCURRENCE	TOTAL % OCCURRENCE	MEAN (ug/L)
Vinyl chloride		11	5	NR
Chloroethane		11	5	NR
Trichlorofluoromethane		11	5	NR
1,1-Dichloroethylene		89	38	11.6
1,1-Dichloroethane		78	33	1.6
Trans-1,2-dichloroethylene	8	78	38	11.7
Chloroform	100	100	100	12.0
1,2-Dichloroethane		33	14	0.6
1,1,1-Trichloroethane	50	100	71	85.1
Carbon tetrachloride	17	56	33	28.4
Bromodichloromethane	100		57	1.6
1,2-Dichloropropane		11	5	NR
Trichloroethylene	100	100	100	25.4
Benzene	75	78	76	1.2
Dibromochloromethane	100		57	1.2
1,1,2-Tetrachloroethane		11	5	NR
1,1,2,2-Tetrachloroethane		22	10	NR
1,1,2,2-Tetrachloroethylene	100	100	100	69.9
Toluene	100	100	100	52.3
Chlorobenzene		33	14	0.9
Ethylbenzene	58	100	76	100.4
2-Chlorophenol	8	11	10	NR
Phenol	25	89	52	135.8
2,4-Dimethylphenol		89	38	74.0
2,4-Dichlorophenol	8	11	10	NR
2,4,6-Trichlorophenol	8	11	10	NR
Pentachlorophenol		44	19	10.1
Dichlorobenzenes	67	44	57	376.5
Naphthalene	58	67	62	50.7
Anthracene/Phenanthrene		33	14	NR
Di-n-butyl phthalate	67	44	57	67.1
Butylbenzyl phthalate	42	67	52	168.2
Bis(2-ethylhexyl) phthalate		56	24	43.0
Di-n-octyl phthalate				
Arsenic	42	44	43	3.2
Cadmium	33	44	38	20.7
Chromium	100	100	100	713.2
Copper	100	100	100	124.8
Lead	100	100	100	323.7
Mercury		78	33	1.9
Nickel	100	100	100	108.7
Silver	75	100	86	150.4
Zinc	100	100	100	860.0
Total Cyanides	58	100	76	90.7
Total Phenols	100	100	100	204.1

NR = Not Reported

TABLE 31. PRIORITY POLLUTANT CONCENTRATIONS IN WASTEWATER FROM SELECTED INDUSTRIES (FROM MEYERS *ET AL*, 1979)

PLANT MANUFACTURING TYPE	1 ORGANICS/PLASTIC	2 ORGANICS/PLASTIC	3 ORGANICS/PLASTIC	4 PHARMACEUTICAL	5 PHARMACEUTICAL	6 PESTICIDE
Metal						
As	12	60	17	<10	<10	20
Cd	3	<1	2	2	<1	<1
Cu	160	32	1100	120	120	130
Cr	650	260	1400	12	12	88
Hg	<1	<5	<0.1	<0.8	<2	<2
Ni	81	36	1600	<10	39	23
Pb	10	27	380	12	22	<10
Zn	770	530	2000	620	41	130
CN	620	<80	4760	<50	250	260
Organics						
Fluorene						
Naphthalene			980			
Pyrene			126			
Phenanthrene/Anthracene						
Acenaphthene						
Acenaphthylene						
Chrysene						
Benzene	405				127	
Methylene chloride			26		47	10400
Chloroform						2240
Trichloroethylene						1620
Toluene						37
Bromoform						56
Ethyl benzene						
2-Nitrophenol	1780	5			123	
4-Nitrophenol	40	24				
Phenol	25	20	680	17		
2,4-Dintrophenol		39				23
2,4-Dimethylphenol		35				
2-Chlorophenol		24				
Pentachlorophenol	53	14		18		
2,4-Dichlorophenol						
2,4,6-Trichlorophenol						

TABLE 31. PRIORITY POLLUTANT CONCENTRATIONS IN WASTEWATER FROM SELECTED INDUSTRIES (FROM MEYERS ET AL, 1979) (cont'd)

PLANT MANUFACTURING TYPE	7 PESTICIDE	8 RUBBER	9 RUBBER	10 WOOD PRESERVER	11 WOOD PRESERVER	12 WOOD PRESERVER
Metal						
As	10	<10	<10	60	530	<10
Cd	2	1	1	<1	<1	<10
Cu	40	22	24	<10	44	45
Cr	51	230	36	16	260	280
Hg	<5	<1.5	<1.2	<0.5	<0.5	<0.6
Ni	510	89	<10	30	22	17
Pb	5	13	10	<5	<10	40
Zn	830	1200	120	160	70	390
CN	40	<50	<50	<20		<50
Organics						
Fluorene					42	
Naphthalene			155	14300		282
Pyrene					570	
Phenanthrene/Anthracene			235		1900	
Acenaphthene				13	400	24
Acenaphthylene					670	
Chrysene					67	
Benzene				187		320
Methylene chloride					32	
Chloroform						
Trichloroethylene						
Toluene		624	35	300	31	695
Bromoform						
Ethyl benzene			29	450	156	56
2-Nitrophenol	17	26				
4-Nitrophenol	103	86	70			
Phenol	5290	1	322	47000	10900	
2,4-Dintrophenol	36	185	183			
2,4-Dimethylphenol					<1	142
2-Chlorophenol			7		<1	
Pentachlorophenol			252	1660	6820	
2,4-Dichlorophenol	2					
2,4,6-Trichlorophenol	4		15	112	420	

refining. In this study, 72-hour composite samples were collected for analysis, and consequently, no estimation of in-plant variability is possible. Two of the three organic chemicals/plastics plants (No. 1 and No. 2) exhibited higher levels of acid extractable (phenolic) compounds in their influents than the third plant, while metal concentrations were higher in the influent wastewater of the third plant than the first two. The wastewaters of the two pharmaceutical plants (No. 4 and No. 5) contained relatively low concentrations of inorganics and organics. One pesticide manufacturer (Plant No. 6) had relatively high levels of chlorinated solvents such as methylene chloride, chloroform and trichloroethylene, whereas the second pesticide manufacturer (No. 7) had no detectable purgeables in the raw wastewater, but elevated levels of phenolic compounds and nickel and zinc. Wastewaters from both rubber manufacturers (Plants 8 and 9) contained principally phenol compounds and metals, although in Plant No. 9, additional purgeables and PAHs were identified. The influent wastewaters from the two wood preserving plants (Nos. 10 and 11), contained a variety of organics including PAHs, purgeables and phenolic compounds. Metal concentrations were not particularly high at these plants. Some purgeable and PAHs were identified in the wastewater from a petroleum refiner (Plant No. 12). Phenol was the only acid extractable compound detected. No metal concentration was exceptionally high.

Summary of Industrial Wastewater Data

Industrial wastewaters tend to contain higher levels of specific contaminants relative to domestic wastewater sampled at pollution control plants. The composition of the wastewater discharged by industries varies widely from one industrial sector to another. When the wastewaters from a number of industries are combined and sampled, however, the contaminant composition tends to be more consistent, as shown by the A.D. Little (1979) study of wastewaters from two industrial areas. In this case, contaminants such as chloroform, trichloroethylene, tetrachloroethylene, toluene, zinc, copper, chromium, nickel and lead were most frequently observed.

3.3 Trace Contaminants in Final Effluents

Data sources reviewed with respect to characterizing final effluents were essentially the same as for influents (i.e. provincial or state authorities, and published literature). The data were reviewed to determine the magnitudes of concentrations, frequency of occurrence in samples, and the variability as identified by the relative standard deviation (RSD) of the mean concentration.

Concentrations of purgeable compounds in grab samples of four Metro Toronto wastewater treatment plant effluents collected in 1985 are reported in Table 32. Dichloromethane was generally the predominant trace organic compound, present in the 15 to 17 ug/L range in three of the four plants. With the exception of tetrachloroethylene at the Highland Creek plant, having a mean concentration of 11.7 ug/L, all other purgeables were present at mean levels of 6 ug/L or lower. Dichloromethane and chloroform were most frequently identified at the four plants, but some organics were regularly found only at one or two plants (e.g. 1,1,1-trichloroethane at Highland Creek, 1,4-dichlorobenzene at Toronto Main and Humber). The effluent from the North Toronto plant had the fewest number of purgeable organic contaminants of the four plants.

TABLE 32. CONCENTRATIONS OF PURGEABLE COMPOUNDS IN METRO TORONTO WPCP EFFLUENTS (METRO TORONTO, 1986)

PURGEABLE COMPOUNDS	TORONTO MAIN				NORTH TORONTO				HIGHLAND CREEK				HUMBER			
	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD ($)	OCCURRENCE ($)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD ($)	OCCURRENCE ($)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD ($)	OCCURRENCE ($)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD ($)	OCCURRENCE ($)
1,1-Dichloroethylene	ND	--	--	0	ND	--	--	0	0.5	1.0	200	25	ND	--	--	0
Dichloromethane	15.6	7.5	48	100	2.6	0.90	35	100	14.9	3.45	23.1	100	16.7	5.53	33.2	100
1,1-Dichloroethane	ND	--	--	0	ND	--	--	0	1.2	0.89	75.6	75	ND	--	--	0
Chloroform	5.0	3.6	72	100	3.1	2.1	66	100	4.0	1.2	29	100	5.7	2.2	39	100
1,1,1-Trichloroethane	ND	--	--	0	ND	--	--	0	4.5	2.2	49	100	1.3	0.55	43	100
Benzene	ND	--	--	0	ND	--	--	0	ND	--	--	0	ND	--	--	0
Bromodichloromethane	ND	--	--	0	0.5	0.6	120	50	ND	--	--	0	ND	--	--	0
Trichloroethylene	ND	--	--	0	ND	--	--	0	0.5	1.0	200	25	ND	--	--	0
Toluene	0.4	0.5	130	50	ND	--	--	0	0.8	0.9	100	75	2.4	3.9	170	50
Tetrachloroethylene	0.3	0.5	200	25	0.3	0.5	200	25	11.7	13.5	116	50	ND	--	--	0
Ethyl benzene	0.1	0.3	200	25	ND	--	--	0	ND	--	--	0	0.25	0.29	120	50
p- and m-Xylene	3.0	2.1	70	75	ND	--	--	0	0.3	0.5	200	50	2.7	2.1	81	75
o-Xylene	0.95	0.91	96	75	ND	--	--	0	ND	--	--	0	1.3	1.0	79	75
1,4-Dichlorobenzene	2.2	0.23	11	100	ND	--	--	0	0.8	1.0	100	50	2.3	0.29	13	100
1,2-Dichlorobenzene	1.5	0.58	38	100	ND	--	--	0	ND	--	--	0	1.0	0.8	80	75

ND = Not Detected
$\bar{X}$ = Arithmetic Mean
S.D. = Standard Deviation of Mean
RSD = Relative Standard Deviation ($ of Mean)
Occurrence = No. of Detections/No. of Tests
No. of grab samples = 4

For all purgeable compounds in Table 32 that were present in 100 percent of samples collected at any one plant, the RSD values were typically less than 50 percent of the mean, which indicated that the concentrations were relatively consistent over the four sampling days. RSD values were higher when at least one reported concentration was below the detection limit.

In the base/neutral extractable fraction of Metro Toronto effluents (Table 33) only bis(2-ethylhexyl) phthalate occurred with mean concentrations greater than 10 ug/L at all four plants, ranging from 14 to 38 ug/L. Bis(2-ethylhexyl) phthalate, di-n-butyl phthalate and 1,4-dichlorobenzene were the most frequently observed base/neutral compounds, detected in all samples at all four treatment plants. For contaminants identified in all samples within one plant, the RSD values ranged from 17 to 133 percent of the mean values. The variability, in terms of RSD, was particularly high for bis(2-ethylhexyl) phthalate at most plants. Variability of the base/neutral extractable compounds was greater than that for purgeable compounds.

Only very low levels of acid extractable compounds were observed in the four Toronto treatment plant effluents. The contaminant 2,4-dimethylphenol was observed most frequently and found in the highest concentrations, as shown in Table 34. The true variability of the phenolic contaminants cannot be estimated because of the low number of detectable concentrations.

Pesticides were detected infrequently in the four Metro Toronto treatment plant effluents (Table 35). Although gamma-BHC (Lindane) was observed most frequently, in approximately half of the samples from each treatment plant, Atrazine had the highest mean concentrations at the Toronto Main and Humber plants. There are insufficient samples with concentrations above the detection limits to evaluate the variability of the pesticides in effluent samples.

The concentrations of trace inorganic contaminants in three Niagara (Ontario) area WPCP effluents are summarized in Table 36. The Welland plant is an activated sludge plant, while Niagara Falls and Fort Erie (Anger Ave.) are primary treatment facilities. In these plant effluents, copper and zinc were generally the predominant metals, although the mean concentration of lead at Welland, at 180 ug/L was the highest of all inorganics in this group of plants. In addition to copper and zinc, low levels of mercury were frequently detected in the 3 treatment plant effluents. The range of RSD values were 34 to 165 percent, suggesting that the contaminant levels in the treatment plant effluents fluctuated widely about the mean value.

Concentrations of purgeable organic compounds in non-chlorinated and chlorinated effluents from three Niagara (Ontario) region WPCPs are summarized in Tables 37, 38 and 39 (Welland, Fort Erie Anger Ave., and Niagara Falls, respectively). The Fort Erie and Niagara Falls pollution control plants were primary treatment facilities, when these samples were collected, whereas the Welland plant is a conventional activated sludge facility. Non-chlorinated effluent samples were collected in 1981 and 1982, while the chlorinated samples were collected in 1983 to 1985. Because of the time difference involved in the two types of samples (i.e. disinfected or not), the data should be interpreted with more caution than if the two effluent sample

TABLE 33. CONCENTRATIONS OF BASE/NEUTRAL EXTRACTABLE ORGANICS IN METRO TORONTO WPCP EFFLUENTS (METRO TORONTO, 1986)

BASE/NEUTRAL EXTRACTABLES	TORONTO MAIN				NORTH TORONTO				HIGHLAND CREEK				HUMBER			
	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)
1,4-Dichlorobenzene	5.1	3.2	63	100	1.6	0.55	34	100	7.0	3.4	49	100	6.0	1.0	17	100
1,2-Dichlorobenzene	3.0	1.9	63	100	1.3	1.8	150	75	2.1	2.3	110	75	3.7	1.1	31	100
Naphthalene	0.6	0.5	90	75	ND	--	--	0	ND	--	--	0	0.4	0.3	70	75
Acenaphthene	ND	--	--	0	ND	--	--	0	ND	--	--	0	ND	--	--	--
Acenaphthylene	ND	--	--	0	ND	--	--	0	ND	--	--	0	ND	--	--	--
Diethyl phthalate	0.7	0.7	100	75	1.8	1.0	55	50	0.5	0.6	120	50	0.5	0.6	120	50
9H Fluorene	ND	--	--	0	0.1	0.3	200	25	ND	--	--	0	ND	--	--	0
Phenanthrene	ND	--	--	0	ND	--	--	0	0.1	0.3	200	25	ND	--	--	0
Anthracene	0.5	0	0	100	1.2	1.3	110	100	0.5	0	0	100	0.9	0.8	90	100
Di-n-butyl phthalate	2.1	0.56	26	100	6.2	3.3	54	100	1.9	0.56	30	100	5.7	2.2	39	100
Fluoranthene	ND	--	--	0	ND	--	--	0	0.3	0.3	120	50	0.1	0.3	200	25
Pyrene	0.3	0.5	200	25	ND	--	--	0	0.8	0.5	70	75	0.3	0.5	200	25
Chrysene	ND	--	--	0	ND	--	--	0	0.5	0.6	120	50	ND	--	--	0
Benzo(a)anthracene	ND	--	--	0	ND	--	--	0	0.5	0.6	120	50	ND	--	--	0
Bis(2-ethylhexyl) phthalate	37.9	50.4	133	100	14.0	9.1	65	100	28.2	8.09	28.7	100	16.4	12.0	79.6	100
Benzo(k)fluoranthene	ND	--	--	0	ND	--	--	0	0.5	0.6	120	50	ND	--	--	0
Benzo(b)fluoranthene	ND	--	--	0	ND	--	--	0	ND	--	--	0	ND	--	--	0
Benzo(a)pyrene	ND	--	--	0	ND	--	--	0	0.3	0.5	200	25	ND	--	--	0

ND = Not Detected
$\bar{X}$ = Arithmetic Mean
S.D. = Standard Deviation of Mean
RSD = Relative Standard Deviation (% of Mean)
Occurrence = No. of Detections/No. of Tests
No. of grab samples = 4

TABLE 34. CONCENTRATIONS OF ACID EXTRACTABLE ORGANICS IN METRO TORONTO WPCP EFFLUENTS (METRO TORONTO, 1986)

ACID EXTRACTABLE	TORONTO MAIN				NORTH TORONTO				HIGHLAND CREEK				HUMBER			
	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)
Phenol	0.6	1.3	200	25	0.6	1.3	200	50	1.3	1.4	120	50	1.3	1.4	120	50
2,4-Dimethylphenol	3.2	2.5	78	100	1.5	0	0	100	1.8	0.7	36	100	4.4	1.3	29	100
p-Chloro-m-cresol	ND	--	--	0	ND	--	--	0	ND	--	--	0	ND	--	--	0
2,4-Dichlorophenol	ND	--	--	0	ND	--	--	0	ND	--	--	0	ND	--	--	0
Pentachlorophenol	1.1	0.8	67	75	1.1	0.8	70	100	1.1	0.8	70	75	1.1	0.75	67	75
o-Cresol	ND	--	--	0	ND	--	--	0	ND	--	--	0	1.0	1.2	120	50
m-Cresol	ND	--	--	0	ND	--	--	0	ND	--	--	0	1.0	1.2	120	50
p-Cresol	ND	--	--	0	ND	--	--	0	ND	--	--	0	ND	--	--	0
2,4,6-Trichlorophenol	ND	--	--	0	ND	--	--	0	ND	--	--	0	ND	--	--	0

$\bar{X}$ = Arithmetic Mean
S.D. = Standard Deviation of Mean
RSD = Relative Standard Deviation (% of Mean)
Occurrence = No. of Detections/No. of Tests
No. of grab samples = 4
ND = Not Detected

TABLE 35. CONCENTRATIONS OF PESTICIDES IN METRO TORONTO WPCP EFFLUENTS (METRO TORONTO, 1986)

PESTICIDE	TORONTO MAIN				NORTH TORONTO				HIGHLAND CREEK				HUMBER			
	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)
Hexachlorobenzene	0.01	0.02	200	25	ND	--	--	0	0.003	0.005	200	25	0.03	0.04	120	50
alpha-BHC	ND	--	--	0	0.003	0.005	200	25	ND	--	--	0	ND	--	--	0
beta-BHC	ND	--	--	0	ND	--	--	0	ND	--	--	0	ND	--	--	0
gamma-BHC	0.02	0.03	120	50	0.04	0.03	80	75	0.03	0.03	100	50	0.02	0.04	120	50
4,4' DDD	ND	--	--	0	0.025	0.050	200	25	ND	--	--	0	ND	--	--	0
4,4'-DDE	0.02	0.05	200	25	0.02	0.05	200	25	ND	--	--	0	ND	--	--	0
Dieldrin	0.02	0.04	200	25	ND	--	--	0	ND	--	--	0	ND	--	--	0
alpha-Endosulfan	ND	--	--	0	0.02	0.05	200	25	ND	--	--	0	ND	--	--	0
Oxychlordane	ND	--	--	0	0.02	0.04	200	25	ND	--	--	0	ND	--	--	0
gamma-Chlordane	ND	--	--	0	ND	--	--	0	ND	--	--	0	ND	--	--	0
Mirex	ND	--	--	0	ND	--	--	0	ND	--	--	0	ND	--	--	0
Atrazine	9.3	18.6	200	25	ND	--	--	0	ND	--	--	0	8.1	16.1	200	25
2,4-D	ND	--	--	0	ND	--	--	0	ND	--	--	0	ND	--	--	0

$\bar{X}$ = Arithmetic Mean
S.D. = Standard Deviation of Mean
RSD = Relative Standard Deviation (% of Mean)
Occurrence = No. of Detections/No. of Tests
No. of grab samples = 4
ND = Not Detected

TABLE 36. CONCENTRATIONS OF TRACE INORGANICS IN NIAGARA (ONTARIO) AREA WPCP EFFLUENTS (MOE, Unpublished)

INORGANIC	WELLAND					FORT ERIE					NIAGARA FALLS				
	n	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	n	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)	n	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCURRENCE (%)
Arsenic	10	4	10	230	30	7	<1	--	--	0	6	<30	--	--	0
Cadmium	11	0.6	2.1	330	9	7	0.002	0.004	190	29	6	0.0004	0.0010	240	17
Chromium	11	5	8	150	56	7	6	7	130	57	6	1	3	240	17
Copper	11	11	19	170	67	7	20	30	110	57	6	33	19	59	100
Mercury	11	0.046	0.100	220	56	7	0.05	0.02	47	86	5	0.038	0.013	34	100
Nickel	11	5	8	170	36	7	3	5	170	29	6	0.8	2	240	17
Lead	11	180	310	170	36	7	4	8	190	29	6	3	5	160	33
Zinc	11	23	35	150	36	7	50	60	110	86	6	29	20	67	83
Cyanide	11	1	3	200	22	7	7	10	130	57	5	16	26	165	80

$\bar{X}$ = Arithmetic Mean

S.D. = Standard Deviation of Mean

RSD = Relative Standard Deviation (% of Mean)

Occurrence = No. of Detections/No. of Tests

Samples are 24 hr composites

TABLE 37. CONCENTRATION OF PURGEABLE COMPOUNDS IN WELLAND (ONTARIO) WPCP EFFLUENT SAMPLES (1981-84) (MOE, Unpublished)

COMPOUND	NON-CHLORINATED EFFLUENT					CHLORINATED EFFLUENT				
	n	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCUR. (%)	n	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCUR. (%)
Dichloromethane	2	4.0	4.8	120	100	4	10	13	130	75
Chloroform	2	1.6	0.28	18	100	4	2.9	1.3	46	100
1,1,1-Trichloroethane	2	0.2	0.3	140	50	4	ND	-	-	0
Chlorodibromomethane	1	0.2	-	-	100	4	ND	-	-	0
Dichlorobromomethane	1	0.2	-	-	100	4	ND	-	-	0
1,1-Dichloroethane	2	0.2	0.2	140	50	4	ND	-	-	0
1,1,2,2-Tetrachloroethane	1	0.3	-	-	100	4	ND	-	-	0
Trichloroethylene	2	0.3	0.4	140	50	4	ND	-	-	0
Tetrachloroethylene	2	1.5	2.0	140	100	4	ND	-	-	0
Benzene	2	1.2	1.7	140	100	4	0.03	0.05	200	25
1,2-Dichlorobenene	1	2.2	-	-	100	4	0.2	0.4	200	25
1,3-Dichlorobenzene	1	1	-	-	0	4	1.0	2.0	200	25
Ethyl benzene	2	0.6	0.8	140	50	4	ND	-	-	0
Toluene	2	3.1	4.2	140	100	4	0.8	1.5	180	25
o-Xylene	2	1.7	220	130	100	4	ND	-	-	0
m-Xylene	2	2.2	3.0	130	100	4	ND	-	-	0

n = No. of samples
$\bar{X}$ = Arithmetic Mean
S.D. = Standard Deviation of Mean
RSD = Relative Standard Deviation (% of Mean)
Occurrence = No. of Detections/No. of Tests
ND = Not Detected

Samples consist of 1 to 4 grabs reduced to a single composite just before analysis

TABLE 38. CONCENTRATIONS OF PURGEABLE COMPOUNDS IN FORT ERIE (ONTARIO) ANGER AVE. WPCP EFFLUENT SAMPLES (1981-85) (MOE, Unpublished)

COMPOUND	NON-CHLORINATED EFFLUENT					CHLORINATED EFFLUENT				
	n	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD ($)	OCCUR. ($)	n	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD ($)	OCCUR. ($)
Chloromethane	1	11.8	-	-	100	NA	-	-	-	-
Dichloromethane	1	ND	-	-	0	8	4.5	9.0	200	38
Chloroform	2	0.6	0.4	70	100	8	14	13	93	100
Bromoform	1	11.8	-	-	100	NA	-	-	-	-
Chlorodibromomethane	1	ND	-	-	0	8	0.5	0.9	190	25
Dichlorobromomethane	2	0.05	0.07	140	50	8	0.2	0.3	190	38
1,2-Dichloroethane	1	0.8	-	-	100	8	0.5	0.7	160	38
1,1,1-Trichloroethane	1	ND	-	-	0	8	12	28	230	50
1,1,2-Trichloroethane	NA	-	-	-	-	8	0.2	0.4	200	25
1,1-Dichloroethylene	NA	-	-	-	-	8	0.3	0.6	180	38
1,2-t-Dichloroethylene	1	0.3	-	-	100	5	110	190	170	60
1,2-c-Dichloroethylene	NA	-	-	-	-	3	0.1	0.06	40	100
Trichloroethylene	2	0.3	0.2	80	100	8	0.4	1.0	250	50
Tetrachloroethylene	2	7.1	6.9	98	100	8	13	27	200	88
1,3-t-Dichloropropylene	NA	-	-	-	-	3	3.3	3.1	92	67
Benzene	2	2.0	0.6	28	100	8	2.1	2.7	130	75
Chlorobenzene	2	0.05	0	0	100	8	0.03	0.05	190	25
1,2-Dichlorobenzene	1	11.3	-	-	100	5	3.9	2.3	59	80
1,3-Dichlorobenzene	NA	-	-	-	-	2	4.0	5.6	140	50
1,4-Dichlorobenzene	NA	-	-	-	-	2	1.0	1.4	140	50
Ethyl benzene	2	3.0	2.8	94	100	8	0.7	0.9	120	75
Toluene	2	7.8	3.0	44	100	8	11	12	110	100
o-Xylene	2	6.4	2.8	44	100	5	0.3	0.3	100	60
m-Xylene	2	6.3	3.3	52	100	5	2.7	4.2	160	100
p-Xylene	NA	-	-	-	-	5	0.3	0.3	100	60

NA = Not Analyzed
n = No. of samples
$\bar{X}$ = Arithmetic Mean
S.D. = Standard Deviation of Mean
RSD = Relative Standard Deviation ($ of Mean)
Occurrence = No. of Detections/No. of Tests
ND = Not Detected

Samples consist of 1 to 4 grabs reduced to a single composite just before analysis

TABLE 39. CONCENTRATIONS OF PURGEABLE COMPOUNDS IN NIAGARA FALLS (ONTARIO) WPCP EFFLUENT SAMPLES (1981-84) (MOE, Unpublished)

COMPOUND	NON-CHLORINATED EFFLUENT					CHLORINATED EFFLUENT				
	n	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCUR. (%)	n	$\bar{X}$ (ug/L)	S.D. (ug/L)	RSD (%)	OCCUR. (%)
Chloromethane	1	13.5	-	-	100	NA	-	-	-	-
Dichloromethane	1	ND	-	-	0	7	5.9	5.8	99	71
Chloroform	2	2.1	0.4	17	100	7	5.3	5.2	97	86
1,1-Dichloroethane	2	0.2	0.2	140	50	7	ND	-	-	0
1,2-Dichloroethane	1	0.2	-	-	100	7	0.9	1.2	140	43
1,1,1-Trichloroethane	2	0.2	0.07	50	100	7	1.7	2.0	120	57
1,1-Dichloroethylene	NA	-	-	-	-	7	0.2	0.4	220	29
1,2-t-Dichloroethylene	1	0.3	-	-	100	7	0.9	1.5	170	43
Trichloroethylene	2	0.4	0.07	20	100	7	ND	-	-	0
Tetrachloroethylene	2	0.9	0.6	63	100	7	1.7	3.7	210	43
Benzene	2	1.8	2.0	110	100	7	0.03	0.08	260	14
Chlorobenzene	2	0.3	0.3	90	100	7	0.01	0.04	260	14
1,2-Dichlorobenzene	1	7.7	-	-	100	4	2.0	2.4	120	50
1,3-Dichlorobenzene	NA	-	-	-	-	3	1.7	2.9	170	33
1,4-Dichlorobenzene	NA	-	-	-	-	3	0.3	0.6	170	33
Ethyl benzene	2	0.4	0.2	60	100	7	0.01	0.04	260	14
Toluene	2	4.1	2.9	72	100	7	1.8	2.0	120	57
o-Xylene	2	1.1	0.9	90	100	4	0.08	0.2	200	25
m-Xylene	2	1.2	0.9	80	100	4	0.08	0.2	200	25
p-Xylene	NA	-	-	-	-	4	0.08	0.2	200	25

NA = Not Analyzed
n = No. of samples
$\bar{X}$ = Arithmetic Mean
S.D. = Standard Deviation of Mean
RSD = Relative Standard Deviation (% of Mean)
Occurrence = No. of Detections/No. of Tests
ND = Not Detected

Samples consist of 1 to 4 grabs reduced to a single composite just before analysis

types were collected at the same time. Because of the almost non-existent database comparing non-chlorinated and chlorinated effluents, however, some trends from these plants have been noted.

At the Welland plant (Table 37), more purgeable compounds were detected in the non-chlorinated effluent samples than the chlorinated effluent. The opposite was true at the two primary treatment plants, where more purgeable compounds were detected in chlorinated effluent samples than non-chlorinated samples. Reaction of chlorine with organic substrates found in primary effluent but not in secondary effluent is a probable explanation for the increased number of compounds in the chlorinated primary effluent.

The mean concentrations of purgeable organics were less than 10 ug/L in the Niagara Falls and Fort Erie primary effluents. The compound 1,2-trans-dichloroethylene was observed at a mean concentration of 110 ug/L in Fort Erie chlorinated effluent (Table 38). The most frequently occurring purgeable compound was at all three WPCPs was chloroform, although certain purgeables were detected regularly at individual plants (e.g. 1,1,1-trichloroethane, toluene and tetrachloroethylene at Fort Erie).

Some concern has been raised about the possibility of chlorination increasing the concentrations of purgeable compounds. At the three Niagara region plants, three compounds (chloroform, dichloromethane and 1,3-dichlorobenzene) had mean concentrations greater in the chlorinated samples than non-chlorinated effluents. This analysis was carried out only on compounds with a mean concentration of greater than 1 ug/L in the chlorinated effluent. Because chloroform and dichloromethane have been implicated as artifacts during laboratory analytical work, their apparent higher concentration in the chlorinated effluent samples may be questioned. This issue has not been raised with 1,3-dichlorobenzene. In the two primary treatment plant effluents, tetrachloroethylene and 1,1,1-trichloroethane had higher mean concentrations in chlorinated compared to non-chlorinated samples.

The database on which to evaluate the impact of chlorination on purgeable compounds in effluents is extremely limited. Based on the Niagara region data, it appears that there is greater potential to increase the number of detectable compounds, and in some cases the mean concentrations of purgeable compounds, during chlorination of primary effluents, than in disinfection of secondary effluents.

Pesticide concentrations in the three Niagara region treatment plant effluents are presented in Tables 40 (Welland), 41 (Fort Erie Anger Ave.) and 42 (Niagara Falls). Mean pesticide concentrations in either chlorinated or non-chlorinated effluent were typically less than 20 ng/L, with the exception of a non-chlorinated effluent sample from the Welland WPCP. In that sample, BHC and chlordane isomers ranged from 27 to 285 ng/L. Few pesticides were detected in all effluents on a regular basis; the compounds gamma-BHC at Welland, and alpha- and gamma-chlordane at Fort Erie were found in more than 80 percent of the total number of effluent samples. With respect to contaminant variability, gamma-BHC in Welland chlorinated effluent displayed the least variability, having an RSD value of 27 percent. The chlordane isomers in Fort Erie chlorinated effluent samples had RSD values in the range of 100 to 110 percent of mean values. The variability of pesticides in non-chlorinated

TABLE 40. PESTICIDE CONCENTRATIONS IN WELLAND (ONTARIO) WPCP EFFLUENT SAMPLES (1981-84) (MOE, Unpublished)

COMPOUND	NON-CHLORINATED EFFLUENT					CHLORINATED EFFLUENT				
	n	$\bar{X}$ (ng/L)	S.D. (ng/L)	RSD ($)	OCCUR. ($)	n	$\bar{X}$ (ng/L)	S.D. (ng/L)	RSD ($)	OCCUR. ($)
α-BHC	1	85	-	-	100	6	1.5	1.2	82	67
β-BHC	1	38	-	-	100	6	ND	-	-	0
γ-BHC	1	27	-	-	100	6	16	4.4	27	100
α-Chlordane	1	289	-	-	100	6	ND	-	-	0
γ-Chlordane	1	135	-	-	100	6	ND	-	-	0
Endosulfan sulphate	1	6.0	-	-	100	6	ND	-	-	0
Hexachlorobenzene	2	8.0	9.9	120	100	6	ND	-	-	0
Aroclor 1016	2	23	32	140	50	6	ND	-	-	0

n = No. of samples
$\bar{X}$ = Arithmetic Mean
S.D. = Standard Deviation of Mean
RSD = Relative Standard Deviation ($ of Mean)
Occurrence = No. of Detections/No. of Tests
ND = Not Detected
Samples are 24 hr composites

TABLE 41. PESTICIDE CONCENTRATIONS IN FORT ERIE (ONTARIO) ANGER AVE. WPCP EFFLUENT SAMPLES (1981-85) (MOE, Unpublished)

COMPOUND	NON-CHLORINATED EFFLUENT					CHLORINATED EFFLUENT				
	n	$\bar{X}$ (ng/L)	S.D. (ng/L)	RSD ($)	OCCUR. ($)	n	$\bar{X}$ (ng/L)	S.D. (ng/L)	RSD ($)	OCCUR. ($)
α-BHC	2	4.0	1.4	35	100	6	1.3	1.2	91	67
γ-BHC	2	7.5	11	140	50	5	3.2	3.6	110	80
α-Chlordane	2	2.5	3.5	140	50	5	13	13	100	100
γ-Chlordane	2	3.0	5.2	140	50	5	16	18	110	100
Heptachlor	2	ND	-	-	0	5	0.4	0.9	200	20
Hexachlorobenzene	2	1.0	0	0	100	5	ND	-	-	0
Aroclor 1248	2	ND	-	-	0	5	5	11	220	20
Aroclor 1254	2	ND	-	-	0	5	25	23	93	60

n = No. of samples
$\bar{X}$ = Arithmetic Mean
S.D. = Standard Deviation of Mean
RSD = Relative Standard Deviation ($ of Mean)
Occurrence = No. of Detections/No. of Tests
ND = Not Detected
Samples are 24 hr composites

TABLE 42. PESTICIDE CONCENTRATIONS IN NIAGARA FALLS (ONTARIO) WPCP EFFLUENT SAMPLES (1981-84) (MOE, Unpublished)

COMPOUND	NON-CHLORINATED EFFLUENT					CHLORINATED EFFLUENT				
	n	$\bar{X}$ (ng/L)	S.D. (ng/L)	RSD (%)	OCCUR. (%)	n	$\bar{X}$ (ng/L)	S.D. (ng/L)	RSD (%)	OCCUR. (%)
α-BHC	1	ND	-	-	0	4	1.8	2.4	140	50
γ-BHC	1	ND	-	-	0	4	9.3	11	120	75
Endosulfan I	1	ND	-	-	0	4	1.5	3	200	25
Hexachlorobenzene	2	1.0	1.4	140	50	4	0.3	0.5	200	25
Methoxychlor	1	ND	-	-	0	4	25	50	200	25
Oxychlordane	1	ND	-	-	0	4	1.0	2.0	200	25
p,p'-DDD	1	ND	-	-	0	4	5	10	200	25
p,p'-DDE	2	0.5	0.7	140	50	4	ND	-	-	0
p,p'-DDT	1	ND	-	-	0	4	1.3	2.5	200	25
Aroclor 1260	2	ND	-	-	0	4	28	55	200	25

n = No. of samples
$\bar{X}$ = Arithmetic Mean
S.D. = Standard Deviation of Mean
RSD = Relative Standard Deviation (% of Mean)
Occurrence = No. of Detections/No. of Tests
ND = Not Detected
Samples are 24 hr composites

samples could not be estimated because of the limited sample size. Similarly, it was not possible to determine the effect of chlorination on number of compounds detected or the magnitude of concentration because of the low number of detectable concentrations.

Concentrations of inorganic contaminants in Ohio POTW effluents are summarized in Table 43. Although zinc was typically the predominant inorganic contaminant, nickel had the highest level of all inorganics at Dayton, and cyanide had the highest level in Marion. Inorganic contaminants were typically higher in Dayton effluent than in the other treatment plant effluents.

TABLE 43. TRACE INORGANIC CONCENTRATIONS IN SELECTED OHIO WASTEWATER TREATMENT PLANT EFFLUENTS (BULZAN, 1986)

INORGANIC	CONCENTRATION (ug/L)				
	MARION	ALLIANCE	LIMA	WAPAKONETA	DAYTON
Arsenic	<4	ND	<5	<4	<2
Cadmium	16	<10	11	2	<10
Chromium	ND	<20	35	4	100
Copper	10	20	<25	14	33
Mercury	ND	ND	0.4	<0.2	<2
Nickel	33	ND	43	17	200
Lead	ND	<50	<5	6	<50
Zinc	101	60	95	44	170
Cyanide	370	<10	1	<10	30

ND = Not Detected

No. of samples = 1 or 2 24-hr composites

Concentrations of organic priority pollutants in seven Ohio treatment plant effluents are presented in Table 44. No individual compound was the predominant contaminant at all POTWs. At the various treatment plants, a number of compounds were detected at levels between 10 and 200 ug/L, including methylene chloride, phenol, bis(2-ethylhexyl) phthalate, di-n-octyl phthalate, and naphthalene. Only the Dayton plant effluent had 3 organic contaminants in the 10 to 100 ug/L range; all other POTW effluents had either one or no compounds in this range.

Table 45 is a compilation of monthly average inorganic contaminant concentrations in five Indiana POTW effluents for the year 1985. Zinc was typically the predominant inorganic in these effluents, with the exception of Crawfordsville. Michigan City had much higher metal and cyanide concentrations than the other cities included in this review. No seasonal variation can be determined from the limited amount of data.

Annual metal concentrations in the effluent from the Madison WI wastewater treatment plant are listed in Table 46. Zinc was the predominant metal with chromium, copper, nickel and lead at substantially lower levels. Cadmium and mercury concentrations were an order of magnitude lower than lead concentrations.

Annual concentrations of cadmium, chromium and copper in two Milwaukee wastewater treatment plants (Jones Island and South Shore) are reported in Table 47. At the Jones Island

TABLE 44. CONCENTRATIONS OF ORGANIC CONTAMINANTS IN SELECTED OHIO WASTEWATER TREATMENT PLANT EFFLUENTS (BULZAN, 1986)

COMPOUND	CONCENTRATION (ug/L)						
	WAPAKONETA	LIMA	TOLEDO	DAYTON	ALLIANCE	COLUMBUS JACKSON PIKE	COLUMBUS SOUTHERLY
1,1,1 Trichloroethane	2.4	8.6		<5			
1,2-t-Dichloroethylene	<1			<5			<10
1,4 Dichlorobenzene	<1						
4-Methyl phenol				<10			
Anthracene			<10				
Benzo(a)anthracene	<1						
Bis(2-ethylhexyl) phthalate	<1	<5	13	40		<10	<10
Butylbenzyl phthalate						<10	
Carbon tetrachloride				<10			
Chloroform	1.4			<10	<5	<10	<10
Chrysene	<1						
Di-n-Butyl phthalate	<1						
Di-n-Octyl phthalate	<1		5	10			
Dichlorobenzenes				<5			
Diethyl phthalate	<1						
Dioctyl phthalate				30			
Ethylbenzene				<5		<10	<10
Methylene chloride	28			<10	<15	<10	4.3
Naphthalene				<2			47
Phenanthrene	<1						
Phenol	<1			80.8		13	3
Pyrene	<1						
Tetrachloroethylene	1.6			<5		<10	
Toluene	<0.9		<10	<5		<10	<10
Trichloroethylene	<2			10		<10	<10

No. of samples = 1 or 2 24-hr composites

TABLE 45. MONTHLY AVERAGE INORGANIC CONTAMINANT CONCENTRATION IN INDIANA TREATMENT PLANT EFFLUENT SAMPLES (BRUMFIELD, 1986)

INORGANIC CONTAMINANT	CITY	MONTHLY METAL CONCENTRATIONS (ug/L)												
		JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEPT	OCT	NOV	DEC	GRAND AVG.
Cadmium	Columbus	0	0	0	0	0	0	0	0	10	0	NR	NR	1
	Crawfordsville	10	10	NR	NR	NR	NR	NR	NR	NR	10	10	10	10
	Elkhart	NR	NR	20	15	10	10	20	10	10	5	10	10	12
	Michigan City	NR	NR	15	15	15	15	10	NR	NR	NR	NR	NR	14
	Speedway (Indianapolis)	1	1	NR	NR	NR	NR	NR	NR	10	10	1	1.5	1
Chromium	Columbus	20	40	30	20	10	10	10	10	20	10	NR	NR	18
	Crawfordsville	50	10	NR	NR	NR	NR	NR	NR	NR	10	10	10	18
	Elkhart	0	100	85	10	30	10	25	40	65	60	55	0	40
	Michigan City	NR	NR	135	145	435	80	165	NR	NR	NR	NR	NR	191
	Speedway	20	27	NR	NR	NR	NR	NR	NR	30	45	15	25	27
Copper	Columbus	20	30	20	20	30	30	20	30	30	20	NR	NR	25
	Crawfordsville	10	10	NR	NR	NR	NR	NR	NR	NR	50	80	40	38
	Elkhart	NR	60	70	65	205	95	85	340	145	80	40	35	111
	Michigan City	NR	NR	70	90	120	65	80	NR	NR	NR	NR	NR	85
	Speedway	50	10	NR	NR	NR	NR	NR	NR	10	13	10	35	21
Mercury	Columbus	0.6	0	0	NR	NR	NR	NR	NR	NR	NR	NR	NR	0.07
	Crawfordsville	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	-
	Elkhart	NR	0.4	0.2	0.2	0.2	0.2	0.2	0.2	0.2	NR	NR	NR	0.23
	Michigan City	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	-
	Speedway	0.5	0.5	NR	NR	NR	NR	NR	NR	0.5	0.5	0.5	0.5	0.5

TABLE 45. MONTHLY AVERAGE INORGANIC CONTAMINANT CONCENTRATION IN INDIANA TREATMENT PLANT EFFLUENT SAMPLES (BRUMFIELD, 1986) (cont'd)

INORGANIC CONTAMINANT	CITY	MONTHLY METAL CONCENTRATIONS (ug/L)												
		JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEPT	OCT	NOV	DEC	GRAND AVG.
Nickel	Columbus	150	100	90	70	60	80	40	50	90	40	NR	NR	77
	Crawfordsville	10	10	NR	NR	NR	NR	NR	NR	NR	80	50	50	40
	Elkhart	NR	100	65	45	50	85	65	60	100	40	45	20	61
	Michigan City	NR	NR	35	135	55	230	85	NR	NR	NR	NR	NR	108
	Speedway	10	10	NR	NR	NR	NR	NR	NR	10	10	15	10	10.8
Lead	Columbus	20	10	10	20	10	30	20	20	20	20	NR	NR	18
	Crawfordsville	10	10	NR	NR	NR	NR	NR	NR	NR	40	20	20	20
	Elkhart	NR	100	60	50	45	20	40	20	30	10	30	15	38
	Michigan City	NR	NR	0	65	40	40	25	NR	NR	NR	NR	NR	34
	Speedway	10	10	NR	NR	NR	NR	NR	NR	0	0	10	10	6.7
Zinc	Columbus	120	180	110	100	110	250	100	90	100	110	NR	NR	124
	Crawfordsville	10	10	NR	NR	NR	NR	NR	NR	NR	45	27	85	35
	Elkhart	NR	305	330	400	195	100	75	775	85	105	75	60	226
	Michigan City	NR	NR	1180	1280	1775	600	940	NR	NR	NR	NR	NR	1155
	Speedway	80	205	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	143
Cyanide	Columbus	25	25	25	NR	NR	NR	NR	NR	NR	NR	NR	NR	25
	Crawfordsville	10	10	NR	NR	NR	NR	NR	NR	NR	70	180	20	58
	Elkhart	NR	10	15	15	10	20	10	10	25	10	10	20	14
	Michigan City	NR	NR	530	160	100	68	55	NR	NR	NR	NR	NR	77
	Speedway	10	15	NR	NR	NR	NR	NR	NR	10	15	10	10	11.7

NR = Not Recorded

No. of samples ranges from 0 to 17

Type of samples not specified

TABLE 46. ANNUAL METAL CONCENTRATIONS IN MADISON, WISCONSIN POTW EFFLUENT (KLEINERT, 1986)

METAL	YEAR	INFLUENT (ug/L)
Cadmium	1979	0.7
	1980	0.4
	1981	0.5
	1982	0.4
	Grand Mean	0.5
Chromium	1979	23
	1980	27
	1981	18
	1982	17
	Grand Mean	21
Copper	1979	7
	1980	11
	1981	12
	1982	12
	Grand Mean	11
Mercury	1979	0.4
	1980	0.5
	1981	0.9
	1982	0.5
	Grand Mean	0.6
Nickel	1979	16
	1980	18
	1981	13
	1982	11
	Grand Mean	15
Lead	1979	4
	1980	6
	1981	6
	1982	5
	Grand Mean	5
Zinc	1979	80
	1980	110
	1981	110
	1982	70
	Grand Mean	90

No. and type of samples not specified

TABLE 47. ANNUAL EFFLUENT CONCENTRATIONS OF SELECTED HEAVY METALS IN MILWAUKEE WASTEWATER TREATMENT PLANTS (KLEINERT, 1986)

METAL	YEAR	JONES ISLAND	SOUTH SHORE
		EFFLUENT (ug/L)	EFFLUENT (ug/L)
Cadmium	1975	16	20
	1976	14	8
	1977	9	7
	1978	9	7
	1979	8	14
	1980	8	7
	1981	8	6
	1982	7	5
	1983	7	5
	Grand Mean	9 ± 3	9 ± 5
Chromium	1975	594	944
	1976	406	520
	1977	215	287
	1978	262	760
	1979	201	187
	1980	118	150
	1981	128	130
	1982	109	77
	1983	149	79
	Grand Mean	242 ± 161	348 ± 320
Copper	1975	107	392
	1976	132	225
	1977	34	151
	1978	64	99
	1979	44	242
	1980	29	53
	1981	33	20
	1982	29	18
	1983	51	17
	Grand Mean	58 ± 37	130 ± 120

No. and type of samples not specified

plant, copper and cadmium levels declined after 1976, while chromium began to decline after 1976, and continued to decline until 1980. Cadmium levels were relatively constant after 1976 at the South Shore plant, but chromium and copper levels declined steadily from 1975 through 1982. The reductions in effluent levels were frequently in response to reduced influent concentrations of these metals, but there is no clear impact of municipal or state pretreatment programs on effluent concentrations. Of the three metals, chromium was the most predominant and cadmium the least.

Concentrations of trace organics in six Wisconsin POTW effluents are summarized in Table 48. The most commonly occurring contaminants were methylene chloride, chloroform and bis(2-ethylhexyl) phthalate. Tetrachloroethylene was observed at 208 ug/L in the Milwaukee South Shore POTW effluent, while 1,1,1-trichloroethane was detected at 50 ug/L in Kenosha effluent. Few contaminants were detected in either the Madison or Green Bay effluent samples.

TABLE 48. ORGANIC CONTAMINANTS IN SELECTED WISCONSIN FINAL EFFLUENTS (KLEINERT, 1986)

COMPOUND	CONCENTRATION (ug/L)					
	JONES ISLAND[1]	SOUTH SHORE[1]	RACINE[2]	MADISON[3]	KENOSHA[2]	GREEN BAY[2]
Methylene chloride	23	67	-	13	90	-
1,2-t-Dichloroethylene	<1	-	<1	-	-	-
Chloroform	5.1	15	7.1	<1	-	40
1,1,1-Trichloroethane	<1	21	9.4	-	50	<1
Trichloroethylene	11	3.4	<1	-	-	<1
Benzene	36	3.8	<1	-	-	-
Toluene	18	4.9	<1	<1	<10	<1
Ethyl benzene	<1	<1	<1	-	-	-
Tetrachloroethylene	-	208	5.8	-	<10	<1
1,3-Dichloropropylene	-	<1	-	-	-	-
Carbon Tetrachloride	-	-	<1	-	-	-
Chlorobenzene	-	-	<1	-	-	-
Chlorodibromomethane	-	-	<1	-	-	-
1,1-Dichloroethane	-	-	<1	-	-	-
1,1-Dichloroethylene	-	-	<1	-	-	-
1,2-Dichloropropane	-	-	<1	-	-	-
Trichlorofluoromethane	-	-	<1	-	-	-
Phenol	<1	-	-	-	-	-
Pentachlorophenol	<1	-	-	-	-	-
1,3-Dichlorobenzene	-	<1	-	-	-	-
1,4-Dichlorobenzene	1.3	<1	2.9	-	-	-
1,2-Dichlorobenzene	<1	<1	-	-	-	-
Diethyl phthalate	7.1	3.4	4.2	-	-	<1
Dimethyl phthalate		<1	-	-	-	-
Di-n-butyl phthalate	1.4	1.6	5.4	-	-	<1
Butylbenzyl phthalate	<1	<1	-	-	-	<1
Bis(2-ethylhexyl) phthalate	19	5.4	6.0	28	30	<1
Naphthalene	<1	<1	-	-	-	-
Fluoranthene	<1	<1	-	-	-	-
Phenanthrene/Anthracene	-	3	-	-	-	-
Fluorene	<1	<1	-	-	-	-
Pyrene	-	<1	-	-	-	-
Chrysene	<1	-	-	-	-	-
Benzo(a)anthracene	-	<1	-	-	-	-
alpha-BHC	-	-	<0.01	-	-	-
Dieldrin	-	-	<0.01	-	-	-
Heptachlor epoxide	-	-	0.14	-	-	-
delta-BHC	-	-	-	-	0.4	-
Endosulfan I	-	-	-	-	<0.2	-
4,4'-DDT	-	-	-	-	0.2	-
Aldrin	-	-	-	-	-	<0.1
Hexachlorobenzene	-	-	-	-	-	<0.1

1. Average of 2 24-hr composite samples.
2. One 24-hr composite sample
3. One 24-hr flow-proportioned composite sample.

The trace organic contaminants identified in two Chicago, IL treatment plant effluents are reported in Table 49. Contaminant levels never exceeded 10 ug/L, and hence, there was no predominant compound in these two influents.

A survey of the EPA priority pollutants in Illinois POTWs was undertaken by the state EPA. The results of the survey are shown in Table 50 for POTW effluents. The most frequently detected organics in this survey were methylene chloride, bis(2-ethylhexyl) phthalate, chloroform, toluene, tetrachloroethylene, diethyl phthalate and 1,1,1-trichloroethane. In these data, only detectable concentrations were used to calculate the mean concentrations and so comparison of these average levels with other data in which non-detectable levels have been included, is not meaningful. Within this study, frequently occurring compounds that were present at high concentrations included methylene chloride, tetrachloroethylene and phenol. Dimethyl phthalate and acrylonitrile also had high mean concentrations but their frequency of detection was very low.

TABLE 49. CONTAMINANT CONCENTRATIONS IN TWO CHICAGO WASTEWATER TREATMENT EFFLUENTS (MSDGC, 1984)

	CONCENTRATION (ug/L)	
	CALUMET	WEST SOUTHWEST PLANT
Methylene chloride	1.2	3.0
Chloroform	2.1	2.6
1,1,1-Trichloroethane	1.7	2.4
Trichloroethylene	<1	2.6
Tetrachloroethylene	2.7	<1
Diethyl phthalate	1.1	1.1
Bis(2-ethylhexyl) phthalate	6.8	3.7

No. and type of samples not specified

The frequency of observation and mean concentration of contaminants measured in effluents in the 40 POTW study are summarized in Table 51. Only twelve contaminants were observed in greater than 50 percent of all effluent samples, including five inorganics, five organic solvents and two phthalates. Contaminants noted at the highest concentrations included cyanide, zinc, methylene chloride, 1,2-dichloroethane, nickel, copper and chromium. The highest mean concentrations belonged to the inorganic contaminants. The majority of the contaminants were observed in less than ten percent of all samples in this major study.

Concentrations of trace contaminants in the effluent of the Moccasin Bend POTW in Nashville, Tennessee during the EPA 30 day study and a previous 6 day study are reported in Table 52. In general, contaminants present in the highest concentrations during the 30 day study were also present in the highest concentrations during the 6 day study. These included chloroform, methylene chloride, toluene, phenol, chromium, nickel, zinc and cyanide. The frequency of occurrence data for these two independent studies is interesting from two aspects:

1) some contaminants which were observed regularly during the six day sampling program were observed less regularly over the 30-day sampling study (e.g. naphthalene, pentachlorophenol, cadmium, lead);

2) some contaminants rarely observed during the 6-day study were detected on a more regular basis during the 30d study (e.g. 1,3-dichlorobenzene, trichlorofluoromethane and fluorene).

TABLE 50. ORGANIC PRIORITY POLLUTANTS IN ILLINOIS WASTEWATER EFFLUENTS (McSWIGGIN, 1986)

COMPOUND	EFFLUENT		COMPOUND	EFFLUENT		COMPOUND	EFFLUENT	
	NO. TIMES DETECTED	MEAN CONC'N (ug/L)		NO. TIMES DETECTED	MEAN CONC'N (ug/L)		NO. TIMES DETECTED	MEAN CONC'N (ug/L)
Acrolein	0	0	Pentachlorophenol	3	1.7	Hexachlorocyclopentadiene	1	1
Acrylonitrile	1	150	2,4,6-Trichlorophenol	2	7.8	Hexachloroethane	1	7
Benzene	12	13.4	Acenaphthene	1	2	Indeno(1,2,3-c,d)pyrene	1	1
Bromoform	2	8.5	Acenaphthylene	1	1	Isophorone	1	20
Carbon tetrachloride	1	1	Anthracene	2	1	Naphthalene	1	1
Chlorodibromomethane	4	7.2	Benzidene	1	1	Nitrobenzene	1	2
Chloroethane	0	0	Benzo(a)anthracene	1	1	n-Nitroso-dimethylamine	1	4
2-Chloroethyl vinyl ether	1	15	Benzo(a)pyrene	2	0.5	n-Nitroso-di-n-propylamine	1	1
Chloroform	18	15.1	Benzo(b)fluoranthene	1	3	n-Nitroso-diphenylamine	1	3
Dichlorobromomethane	9	20.3	Benzo(g,h,i)perylene	1	2	Phenanthrene	1	2
Dichlorodifluoremethane	0	0	Benzo(k)fluoranthene	1	3	Pyrene	2	0.5
1,1-Dichloroethane	1	1	Bis(2-chloroethoxy) methane	2	10.5	1,2,4-Trichlorobenzene	1	5
1,2-Dichloroethane	1	2.2	Bis(2-chloroethyl) ether	1	4	Aldrin	3	0.015
1,1-Dichloroethylene	0	0	Bis(2-chloroisopropyl) ether	1	1	alpha-BHC	11	0.092
1,2-Dichloropropane	0	0	Bis(2-ethylhexyl) phthalate	22	31.7	beta-BHC	3	0.115
1,3-Dichloropropylene	0	0	4-Bromophenyl phenyl ether	1	1	delta-BHC	9	0.08
Ethyl benzene	6	5.8	Butylbenzyl phthalate	3	4.4	gamma-BHC (Lindane)	8	0.06
Methyl bromide	0	0	2-chloronaphthalene	1	1	Chlordane	3	0.47
Methyl chloride	2	34	4-chlorophenyl phenyl ether	1	3	4,4'-DDT	4	0.29
Methylene chloride	25	470	Chrysene	1	1	4,4'-DDE	2	0.030
1,1,2,2-Tetrachloroethane	2	6.5	Dibenzo(a,h)anthracene	1	6	4,4'-DDD	2	0.020
Tetrachloroethylene	16	116	1,2-Dichlorobenzene	1	3	Dieldrin	2	0.020
Toluene	17	17.6	1,3-Dichlorobenzene	1	2	alpha-Endosulfan	3	0.010
1,2-t-Dichloroethylene	1	0.2	1,4-Dichlorobenzene	1	2	beta-Endosulfan	4	0.100
1,1,1-Trichloroethane	15	9.0	3,3'-Dichlorobenzidine	1	15	Endosulfan sulfate	2	0.21
1,1,2-Trichloroethane	1	6	Diethyl phthalate	16	11.2	Endrin	2	0.050
Trichloroethylene	7	19.2	Dimethyl phthalate	3	141	Endrin aldehyde	2	0.500
Trichlorofluoromethane	0	0	Di-n-butyl phthalate	12	2.2	Heptachlor	3	0.120
Phenol	7	112	2,4-Dinitrotoluene	1	1	Heptachlor epoxide	3	0.030
2-Chlorophenol	1	20	2,6-Dinitrotoluene	1	2	Aroclor 1016	2	0.06
2,4-Dichlorophenol	1	14	Di-n-octyl phthalate	1	2	Aroclor 1221	2	0.06
2,4-Dimethyl phenol	2	6.5	1,2-Diphenylhydrazine	1	61	Aroclor 1232	2	0.06
4,6-Dinitro-o-cresol	2	34	Fluoranthene	2	0.6	Aroclor 1242	2	0.06
2,4 Dinitrophenol	2	57	Fluorene	1	1	Aroclor 1248	3	1.0
2-Nitrophenol	1	30	Hexachlorobenzene	1	4	Aroclor 1254	2	0.41
4-Nitrophenol	1	30	Hexachlorobutadiene	1	5	Aroclor 1260	1	2.0
p-chloro-m-cresol	1	16				Toxaphene	2	2.55

Total no. of samples not specified

TRACE CONTAMINANT CHARACTERIZATION DATA

TABLE 51. OCCURRENCE AND CONCENTRATION OF PRIORITY POLLUTANTS IN EFFLUENTS DURING 40 POTW STUDY (EPA, 1982a)

PARAMETER	NUMBER OF SAMPLES ANALYZED	PERCENT OF SAMPLES WHERE DETECTED	MEAN CONCEN-TRATION	PARAMETER	NUMBER OF SAMPLES ANALYZED	PERCENT OF SAMPLES WHERE DETECTED	MEAN CONCEN-TRATION
Cyanide	276	97	157 ug/L	Phenanthrene	302	3	0.3 ug/L
Zinc	289	94	169 ug/L	Anthracene	302	3	0.3 ug/L
Copper	289	91	38 ug/L	Bromoform	302	3	0.1 ug/L
Methylene chloride	302	86	362 ug/L	2,4,6-Trichlorophenol	302	3	<0.1 ug/L
Chromium	289	85	34 ug/L	1,1,2-Trichloroethane	302	3	0.1 ug/L
Bis(2-ethylhexyl) phthalate	302	84	22 ug/L	1,1,2,2-Tetrachloroethane	302	3	<0.1 ug/L
Chloroform	302	82	8 ug/L	1,4-Dichlorobenzene	302	3	0.1 ug/L
Tetrachloroethylene	302	79	20 ug/L	2-Nitrophenol	302	3	<0.1 ug/L
Nickel	289	75	65 ug/L	Aldrin	303	3	33 ng/L
Toluene	302	53	12 ug/L	delta-BHC	303	3	12 ng/L
Di-n-butyl phthalate	302	52	4 ug/L	Chrysene	302	2	0.1 ug/L
1,1,1-Trichloroethane	302	52	29 ug/L	Dimethyl phthalate	302	2	<0.1 ug/L
Trichloroethylene	302	45	7 ug/L	Vinyl chloride	302	2	3 ug/L
gamma-BHC	303	33	56 ng/L	1,2-Benzanthracene	302	2	0.3 ug/L
Mercury	288	31	136 ng/L	1,3-Dichlorobenzene	302	2	0.1 ug/L
Phenol	302	29	1 ug/L	beta-BHC	303	2	9 ng/L
Cadmium	289	28	13 ug/L	Thallium	289	2	<0.1 ug/L
Silver	289	25	1 ug/L	Acenaphthene	302	2	<0.1 ug/L
Ethyl benzene	302	24	0.9 ug/L	Heptachlor	303	2	8 ng/L
Benzene	302	23	1 ug/L	Heptachlor epoxide	303	2	4 ng/L
Lead	289	21	16 ug/L	4-Nitrophenol	302	2	0.4 ug/L
Pentachlorophenol	301	21	7 ug/L	Beryllium	289	1	<0.1 ug/L
Dichlorobromomethane	302	16	0.5 ug/L	Methyl bromide	302	1	1 ug/L
Diethyl phthalate	301	13	0.5 ug/L	Pyrene	302	1	<0.1 ug/L
1,2-trans-Dichloroethylene	302	13	0.9 ug/L	PCB-1242	303	1	43 ng/L
Antimony	288	13	2 ug/L	Acenaphthylene	302	1	<0.1 ug/L
Arsenic	289	12	2 ug/L	Fluoranthene	302	1	<0.1 ug/L
Butylbenzyl phthalate	302	11	0.7 ug/L	Hexachlorobenzene	302	1	<0.1 ug/L
Selenium	289	10	2 ug/L	Isophorone	302	1	<0.1 ug/L
1,1-Dichloroethylene	302	10	0.3 ug/L	Parachlorometa cresol	302	1	<0.1 ug/L
Chlorodibromomethane	302	8	0.2 ug/L	4,4-DDD	303	1	2 ng/L
1,2-Dichlorobenzene	302	8	0.6 ug/L	Indeno(1,2,3-c,d)pyrene	296	1	<0.1 ug/L
1,2-Dichloroethane	302	8	156 ug/L	Dichlorodifluoromethane	302	1	0.5 ug/L
1,1-Dichloroethane	302	8	0.3 ug/L	Fluorene	302	1	<0.1 ug/L
alpha-BHC	303	8	18 ng/L	2-Chlorophenol	302	1	<0.1 ug/L
Methyl Chloride	302	7	14 ug/L	2,4-Dinitrotoluene	302	1	<0.1 ug/L
Carbon Tetrachloride	302	6	1 ug/L	3,3-Dichlorobenzidine	302	1	<0.1 ug/L
Naphthalene	302	6	0.4 ug/L	1,12-Benzoperylene	295	LT 1	<0.1 ug/L
2,4-Dichlorophenol	302	4	0.1 ug/L	1,2:5,6-Dibenzanthracene	296	LT 1	<0.1 ug/L
1,2-Dichloropropane	302	4	<0.1 ug/L	4,6-Dinitro-o-cresol	301	LT 1	<0.1 ug/L
1,2,4-Trichlorobenzene	302	4	2 ug/L	Chloroethane	302	LT 1	<0.1 ug/L
Di-n-octyl phthalate	302	4	0.3 ug/L	1,2-Diphenylhydrazine	302	LT 1	<0.1 ug/L
Trichlorofluoromethane	302	4	0.2 ug/L	Chlordane	303	LT 1	<1 ng/L
2,4-Dimethylphenol	302	4	0.2 ug/L	Dieldrin	303	LT 1	<0.1 ng/L
Chlorobenzene	302	3	0.1 ug/L	PCB-1254	303	LT 1	6 ng/L

* Pollutants not listed were never detected.

* Occurrences are based on all secondary effluent samples taken.

* Pollutants reported as less than the detection limit and unconfirmed pesticides are assumed not detected.

TABLE 52. COMPARISON OF SIX-DAY AND THIRTY-DAY SECONDARY EFFLUENT PRIORITY POLLUTANT CONCENTRATION AND OCCURRENCE DATA (EPA, 1982b)

PARAMETER	SIX-DAY STUDY				THIRTY-DAY STUDY			
	PERCENT OCCURRENCE	AVERAGE CONCEN-TRATION (ug/L)	MAXIMUM CONCEN-TRATION (ug/L)	MINIMUM CONCEN-TRATION (ug/L)	PERCENT OCCURRENCE (ug/L)	AVERAGE CONCEN-TRATION (ug/L)	MAXIMUM CONCEN-TRATION (ug/L)	MINIMUM CONCEN-TRATION (ug/L)
Benzene	100	2	3	1	100	4	18	1
1,1,1-Trichloroethane	80	2	2	ND	50	5	65	ND
Chloroform	100	24	40	19	100	37	62	11
Ethylbenzene	60	1	3	ND	60	4	22	ND
Methylene chloride	100	11	31	5	100	82	820	14
Tetrachloroethylene	100	2	3	1	63	7	43	ND
Toluene	100	56	180	11	97	34	670	ND
Trichloroethylene	20	<1	1	ND	63	4	58	ND
Pentachlorophenol	67	3	7	ND	7	<1	2	ND
Phenol	100	29	76	1	93	60	520	ND
1,2,4-Trichlorobenzene	100	8	16	3	63	6	48	ND
1,2-Dichlorobenzene	33	1	2	ND	3	1	25	ND
1,4-Dichlorobenzene	0	ND	ND	ND	20	1	11	ND
Naphthalene	100	8	24	1	10	1	15	ND
Bis(2-ethylhexyl) phthalate	100	8	25	2	47	10	220	ND
Di-n-butyl phthalate	100	2	3	1	30	2	19	ND
Diethyl phthalate	100	3	6	1	50	6	37	ND
Phenanthrene	17	<1	2	0	0	ND	ND	ND
Antimony	100	6	8	1	7	<1	10	ND
Arsenic	100	4	6	1	7	1	14	ND
Cadmium	100	6	7	5	13	2	29	ND
Chromium	100	56	69	10	90	51	430	ND
Copper	83	10	20	ND	67	21	140	ND
Cyanide	100	115	160	72	100	88	603	12
Lead	83	64	90	ND	10	5	57	ND
Nickel	100	82	103	66	50	39	170	ND
Selenium	100	3	5	2	0	ND	ND	ND
Silver	100	2	3	1	83	1	5	ND
Thallium	100	1	2	1	0	ND	ND	ND
Zinc	100	94	121	77	100	100	200	ND
1,2-trans-Dichloroethylene	0	ND	ND	ND	0	ND	ND	ND
2,4-Dichlorophenol	83	2	3	ND	60	3	17	ND
Butylbenzyl phthalate	33	1	3	ND	0	ND	ND	ND
Chlorobenzene	0	ND	ND	ND	7	<1	2	ND
2,4,6-Trichlorophenol	67	2	3	ND	13	<1	6	ND
alpha-Endosulfan*	0	ND	ND	ND	0	ND	ND	ND
gamma-BHC*	17	233	1400	ND	0	ND	ND	ND
1,3-Dichlorobenzene	0	ND	ND	ND	50	2	11	ND
Fluoranthene	0	ND	ND	ND	3	<1	ND	ND
Mercury*	0	ND	ND	ND	7	20	300	ND
Trichlorofluoromethane	0	ND	ND	ND	17	<1	5	1
2,4-Dimethylphenol	33	3	10	ND	37	3	17	ND
Acenapthalene	50	2	7	ND	17	<1	43	ND
Di-n-octyl phthalate	0	ND	ND	ND	10	3	57	ND
Dimethyl phthalate	33	1	2	ND	10	6	28	ND
Fluorene	0	ND	ND	ND	11	<1	1	ND
2-Chlorophenol	0	ND	ND	ND	6	<1	1	ND
1,1-Dichloroethylene	0	ND	ND	ND	6	<1	3	ND
4-Nitrophenol	0	ND	ND	ND	6	1	31	ND
Bis(2-chloroethoxy) methane	0	ND	ND	ND	3	<1	4	ND
Acenaphthylene	0	ND	ND	ND	3	<1	2	ND
Parachlorometa cresol	0	ND	ND	ND	3	<1	3	ND
1,1,2-Trichloroethane	0	ND	ND	ND	3	<1	2	ND
1,1,2,2-Tetrachloroethane	0	ND	ND	ND	3	<1	3	ND
2-Nitrophenol	0	ND	ND	ND	3	<1	1	ND

ND = Not Detected

< = Less Than

> = Greater Than

* = Mercury and pesticide concentrations are in ng/L.

Pollutants not listed were not detected.

The implication from this comparison is that a study with a small number of data points may not be sufficient to adequately characterize certain wastewater trace contaminants. Composite samples do not accurately reflect contaminant variability.

Concentrations of contaminants in the effluents of two POTWs examined for the EPA Report to Congress (EPA, 1986) are summarized in Table 53. Treatment plant 1001 had detectable levels of cadmium, zinc, 1,1,1-trichloroethane and several pesticides, whereas the only contaminants detected in the effluent of plant 1002 were chromium, lead, delta-BHC and gamma-BHC.

TABLE 53. CONCENTRATIONS OF CONTAMINANTS IN TWO POTW EFFLUENTS (EPA, 1986)

CONTAMINANT	EFFLUENT CONCENTRATION	
	PLANT 1001	PLANT 1002
Cadmium	8	<5
Chromium	<10	18
Lead	<5	43
Zinc	17	<20
delta-BHC	0.242	0.009
gamma-BHC	<0.004	0.089
4,4'-DDD	0.423	<0.011
Pronamide	0.233	<0.010
Trichlorfon	0.233	<0.003
1,1,1-Trichloroethane	13	<10

No. and type of samples not specified.

In a study of selected contaminants in the effluent of the Hamilton, Ontario WPCP (CANVIRO Consultants Ltd., 1984a), metals were present at concentrations in the 10 to 90 ug/L range (except mercury), while PAHs were typically detected in the 0.10 to 0.80 ug/L range (Table 54). Lindane, total PCBs and pentachlorophenol were observed at the 0.01 to 0.10 ug/L level.

TABLE 54. CONCENTRATIONS OF CONTAMINANTS IN THE HAMILTON, ONTARIO WPCP EFFLUENT (CANVIRO Consultants Ltd., 1984a)

CONTAMINANT	CONCENTRATION (ug/L)	CONTAMINANT	CONCENTRATION (ug/L)
Chromium	20	Naphthalene	0.3
Copper	20	Acenaphthalene	0.04
Mercury	0.03	Dibenzofuran	0.12
Nickel	40	Fluorene	0.19
Lead	10	Fluoranthene	0.61
Zinc	90	Carbazole	0.41
Lindane	0.01	Pyrene	0.80
Total PCBs	0.03	Benzo(a)pyrene	0.62
Pentachlorophenol	0.10		

No. of samples = 28 x 24-hr composite samples

The concentrations of heavy metals in the effluent of the Edmonton Gold Bar Wastewater Treatment Plant are summarized in Table 55 (Neilsen, 1982). Zinc and nickel were the contaminants with the highest mean concentrations at 220 ug/L and 90

TABLE 55. CONCENTRATIONS OF TRACE METALS IN THE EDMONTON, ALBERTA GOLD BAR WPCP EFFLUENT (NEILSEN, 1982)

DAY	TIME	METAL CONCENTRATION (ug/L)				
		Cd	Cr	Cu	Ni	Zn
1	1756	14	18	15	543	580
2	0530	4	28	9	146	190
3	1644	3	10	10	39	250
4	0415	1	10	8	21	190
5	1652	2	23	14	25	190
6	0416	3	20	14	18	140
7	1623	4	35	14	20	120
8	418	4	20	11	28	140
9	1615	2	13	12	30	310
9	2215	2	20	12	33	130
MEAN (ug/L)	-	4	20	12	90	220
RSD (%)	-	94	40	20	180	62

Samples were 24-hr composites

ug/L, respectively. Nickel and cadmium were the most variable metals (based on RSD), due to particularly high concentrations detected on the first sampling date. Copper was the least variable of the metals in the effluent.

The levels of metals and phenol in a Puerto Rican secondary treatment plant effluent are presented in Table 56 (Roman-Seda, 1984). Zinc, at 480 ug/L, was significantly higher in concentration than the other metals. Phenol was present at a mean concentration of 107 ug/L. All contaminants exhibited the same magnitude of variation, with RSD values ranging from 52 percent for zinc to 80 percent for chromium and lead.

TABLE 56. CONCENTRATION OF CONTAMINANTS IN A PUERTO RICAN WPCP SECONDARY EFFLUENT (ROMAN-SEDA, 1984)

CONTAMINANT	COPPER	CHROMIUM	LEAD	ZINC	PHENOL
Mean Concentration (ug/L)	30	40	40	48	107
RSD (%)	70	80	80	52	61

No. of 24-hr composite samples = 33

The physical/chemical state of metal contaminants in wastewater treatment plant effluents has received some attention, because tertiary processes may be required to reduce effluent concentrations. In Seattle, WA POTW effluent, most of the copper complexing agents in the secondary effluent were soluble (i.e. passed through a 0.45 um filter), and hence, the copper was found mainly in the soluble state (Buckley, 1983). In a different secondary effluent sample, 76 percent of cadmium, 67 percent of copper and only 25 percent of lead were present in the effluent fraction passing through a 0.4 um filter (Laxen and

Harrison, 1981). Lawson et al (1984) indicated that in activated sludge effluents, nickel and copper were predominantly associated with organic compounds in the 5,000 to 10,000 molecular weight range. It was also concluded by Buckley (1983) that 67 percent of the organic compounds complexed with copper had weights of 10,000 or less. In another secondary effluent, copper and nickel were found primarily in soluble form, whereas cadmium, chromium, zinc and lead were not (Rossin et al, 1982). Tertiary processes such as effluent filtration may reduce concentrations of certain metals such as lead, but would be less effective for other metals such as nickel and copper.

Summary of Effluent Data

The contaminants which occur most frequently in wastewater treatment plant effluents are metals (e.g. zinc, copper, chromium), purgeable compounds (mainly chlorinated solvents such as methylene chloride, chloroform, tetrachloroethylene), and phthalate esters such as bis(2-ethylhexyl) phthalate and di-n-butyl phthalate. Metal concentrations are generally higher than organic concentrations although in some site-specific locations, a few individual organics may have higher levels than the metals in the effluents.

Concentrations of trace metal contaminants were typically lower in Canadian WPCP effluents than in American treatment plant effluents. Trace metal concentrations in the three Niagara (Ontario) region treatment plants were among the lowest noted in this study, despite two of the facilities being primary treatment plants. Concentrations of nickel and zinc in the Edmonton Gold Bar WPCP effluent contained elevated levels of nickel and zinc relative to the Niagara plant effluents on the Hamilton, Ontario WPCP effluent. The range of chromium, copper and zinc concentrations was higher in U.S. effluents than Canadian WPCP effluents.

In both Canadian and U.S. treatment plant effluents, trace organic concentrations were usually less than 10 ug/L, with the exception of dichloromethane and bis(2-ethylhexyl) phthalate, which were often present at concentrations between 10 and 100 ug/L. These two compounds may be artifacts of sampling and analysis.

Effluent variability data is rather limited, but there are some indications that contaminant concentrations fluctuate widely about the mean value or higher even after biological treatment. RSD values of 100 percent of the mean or greater have been reported, but these are often associated with a small sample population and/or concentrations near the detection limit.

3.4 Trace Contaminants in Sludges and Other Internal Recycle Streams

3.4.1 Sludges

In Canada, most of the sludge characterization data concerns metals and a substantial body of information about these levels, particularly in Ontario sludge, has been published.

TRACE CONTAMINANT CHARACTERIZATION DATA

Five anaerobically digested sludges in Ontario were analyzed to establish a sampling methodology for adequately characterizing sludges (Monteith and Stephenson, 1978). Grab samples were collected in all cases. The metals data are summarized in Table 57. Zinc had the highest concentration of metals in the sludges ranging from 920 to 2,510 ug/g (dry weight basis). Copper and lead had approximately equal concentration ranges and were lower than zinc. Cadmium and nickel concentrations were the lowest observed in these sludges. Simcoe digested sludge contained a high level of cadmium when the sludge was sampled.

TABLE 57. METAL CONCENTRATIONS IN FIVE ANAEROBICALLY DIGESTED SLUDGES IN ONTARIO (MONTEITH AND STEPHENSON, 1978)

MUNICIPALITY	NO. OF SAMPLES*	METAL CONCENTRATION (ug/g)				
		Cd	Cu	Ni	Pb	Zn
Simcoe	198	77.7	582	34.7	452	2,510
Chatham	225	2.53	405	132	456	1,810
Milton	254	--	631	29.5	303	893
Oakville S.E.	147	--	860	30.3	630	920
Tillsonburg	40	9.1	899	24	230	1,330

* Grab samples

Concentrations of metals in the sludges from six Ontario activated sludge treatment plants are reported in Table 58 (Atkins and Hawley, 1978). Sludge from the Hamilton treatment plant, located in a heavily industrialized area, contained much higher metal concentrations (except mercury) than sludges from the other treatment plants. In this study copper and zinc were the metals present at the highest concentrations, although the sludge from Barrie had an elevated level of chromium at 12,300 ug/g (dry weight).

TABLE 58. METAL CONCENTRATIONS IN SLUDGES FROM SIX ONTARIO ACTIVATED SLUDGE PLANTS (ATKINS AND HAWLEY, 1978)

MUNICIPALITY	NO. OF* SAMPLES	METAL CONCENTRATION (ug/g)							
		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Burlington (Elizabeth Gardens)	2	3	<3	<13	740	1.4	<70	200	404
Fergus	2	6	0.5	180	850	0.14	8.2	11	780
Barrie	1	3	0.8	12300	700	1.2	450	374	49
Guelph	2	14	8.8	100	143	0.13	4.3	73	275
Mississauga (Lakeview)	2	6.3	4	<0.7	60	2.8	13	52	22
Hamilton	1	20	25	3300	1200	0.62	440	1600	8500

* Samples are 4-hr composites

Concentrations of metals and PCBs (total) have been examined in sludges applied to agricultural sites in Ontario. Although zinc generally had the highest concentration of the metals, as shown in Table 59, copper, chromium and lead also were present at levels that were frequently close to that of

TABLE 59. METAL AND PCB CONCENTRATIONS IN WASTEWATER SLUDGES APPLIED AT 10 AGRICULTURAL SITES IN ONTARIO (WEBBER *ET AL*, 1983)

	METAL CONCENTRATION (ug/g)							
SLUDGE SOURCE	Cd	Zn	Cu	Ni	Pb	Cr	As	Hg	PCBs
Brantford	23	2200	1240	199	1230	697	16.1	3.1	0.528
Burlington[a] (Skyway)	214	5060	1360	403	1240	1780	36.1	4.0	1.61
Galt	54	1490	1180	53	305	1270	9.7	5.5	0.156
Georgetown	47	646	556	51	1190	316	3.9	2.4	0.279
Guelph	206	7220	3680	88	1440	3910	13.1	15.6	0.715
Kingston	7.5	1780	626	26	893	1380	7.2	10.5	0.821
Kitchener	12.3	6610	658	333	615	6980	9.9	3.1	0.651
Oakville (Southwest)	45	6820	1510	338	1350	2010	7.3	8.0	0.396
Oshawa (Harmony Creek)	7.3	6100	683	1120	1340	6560	19.8	3.3	0.130
Stratford	33	2740	1180	1260	956	1540	17.7	3.4	0.227

a. All sludges were secondary digested except for Burlington, which was waste activated.

b. 3 replicate grab samples were collected once at each site.

zinc (Webber et al, 1983). Mercury and arsenic had the lowest concentrations of the metals tested, in the range of 2 to 36 ug/g. Total PCBs ranged between 0.13 and 1.6 ug/g in the sludges.

The difference in metal concentrations in sludge samples from the Guelph treatment plant reported by these two studies is over an order of magnitude. Samples in the two studies were collected at least two years apart. The difference in concentrations may be due to sample collection and preparation techniques, as well as highly variable metal inputs. The differences in concentrations in sludge from the same plant emphasize the highly variable nature of sludge contaminant concentrations.

Metal concentrations in five Ohio treatment plant sludges are compiled in Table 60. The highest metal concentrations were noted for zinc, copper and chromium, with zinc levels generally predominating. At 86 ug/g, cadmium was observed at an elevated level in the Dayton sludge.

TABLE 60. METAL CONCENTRATIONS IN SELECTED OHIO TREATMENT PLANT SLUDGES (BULZAN, 1986)

INORGANIC	CONCENTRATION* (ug/g)				
	MARION	ALLIANCE	LIMA	WAPAKONETA	DAYTON
Arsenic	11	<3	<0.19	6	0.3
Cadmium	5	10	1.2	5.9	86
Chromium	110	68	120	400	1100
Copper	270	1970	27	400	860
Mercury	2.7	3.0	0.15	1.3	1.7
Nickel	44	59	36	150	250
Lead	150	470	74	220	300
Zinc	480	2120	260	550	2800

* Except Lima, in ug/L

No. of samples = 1 or 2 (sample type not identified)

Concentrations of extractable trace organic contaminants in four digested sludges (3 from Ontario and one from Manitoba) are summarized in Table 61 (Environment Canada, Unpublished). Digested sludge from Hamilton, Ontario had the greatest number of contaminants, and the highest levels of contaminants, of the four sludges. The principal classes of contaminants were PAHs and phthalates in Hamilton sludge, as well as in the North Toronto digested sludge sample. Contaminants identified in the Winnipeg N.E. sludge were all acid extractable (phenolic) compounds. Few organics were identified in the Elmira, Ontario sludge and these were mainly phthalates.

Selected Ohio sludges have also been analyzed for trace organic contaminants, and the results of these tests are summarized in Table 62. The most prevalent compounds included methylene chloride, toluene, ethyl benzene and bis(2-ethylhexyl) phthalate. Although most of the contaminant concentrations were on the order of 2 ug/g or less, a number of very high levels were observed, particularly in the Wapakoneta and Alliance sludges. Only toluene and xylenes were detected in the Marion plant sludge while no organic priority pollutants were detected in the Lima treatment plant sludge.

TABLE 61. ORGANIC CONTAMINANT CONCENTRATIONS IN SELECTED CANADIAN SLUDGES (ENVIRONMENT CANADA, Unpublished)

CONTAMINANT	CONCENTRATION (ug/g)			
	NORTH TORONTO DIGESTED	HAMILTON DIGESTED	ELMIRA DIGESTED	WINNIPEG N.E DIGESTED
Chlorophenol				1.4
2,4-Dichlorophenol				2.6
4,6-Dinitro-o-cresol				13.5
Nitrophenol				13.0
Pentachlorophenol				5.4
2,4,6-Trichlorophenol				8.2
Acenaphthylene		47		
Anthracene		114		
Phenanthrene	1	593		
Chrysene		39		
Benzo(k)fluoranthene		43		
Benzo(a)pyrene		28		
Fluoranthene	2	232		
Fluorene	2	98		
Naphthalene	2	45		
Pyrene	3	171		
1,4-Dichlorobenzene	1			
N-Nitrosodiphenylamine	3	4	43	
N-Nitrosodi-n-propylamine	2			
Di-n-butyl phthalate	38	20	430	
Dimethyl phthalate	2			
Di-n-octyl phthalate	6			
Bis(2-ethylhexyl) phthalate	215	26	92	
Bis(2-chloroisopropyl) ether	1			
4,6-dinitrotoluene	4			
Dibenzofuran		61		
Carbazole		43		

No. of samples = 1 grab for North Toronto, Hamilton and Elmira
= 1 weekly composite for Winnipeg, N.E.

TABLE 62. ORGANIC CONTAMINANT CONCENTRATIONS IN SELECTED OHIO TREATMENT PLANT SLUDGES (BULZAN, 1986)

CONTAMINANT	CONCENTRATION						
	WAPAKONETA (ug/g)	TOLEDO (ug/L)*	DAYTON (ug/g)	ALLIANCE (ug/g)	JACKSON PIKE COMB. DIG. & CENTRIF. (ug/g)	COLUMBUS SOUTHERLY (ug/g)	MARION WWTP (ug/g)
1,1-Dichloroethene			0.1				
1,2-t-Dichloroethylene						0.5	
1,4-Dichlorobenzene	188						
2-Methyl phenol			0.3				
3,4-Benzofluoranthene					0.63		
Acrolein			361				
Anthracene			1.7		2.4	0.83	
Benzene						0.14	
Benzo(a)anthracene					1.6	0.79	
Benzo(k)fluoranthene					0.63		
Butylbenzyl phthalate					13.	2.0	
Bis(2-ethylhexyl) phthalate	14000	3000	17.		54.	14.	
Chlordane				1.9	5.2		
Chlorobenzene			1.1	160.			
Chrysene					1.6	0.79	
Di-n-butyl phthalate			1.2				
Di-n-octyl phthalate					16.	0.54	
Dichlorobenzenes			1.6				
Diethyl phthalate			0.4				
Dioctyl phthalate			31.				
Ethylbenzene	0.19	16	0.87	28.	0.84	0.11	
Fluoranthene					1.6	0.71	
g-BHC							
Methyl chloride		27					
Methylene chloride	0.66	32000	0.24	440.	0.28	0.29	
Naphthalene	159		0.				
PCB 1254				0.36			
Phenanthrene					2.4	0.83	
Phenol	244		1.1			2.5	
Pyrene					1.7	0.71	
Tetrachloroethylene			0.3			0.07	
Toluene	0.62	26	0.46	520.	8.8	1.6	4.0
Trichloroethylene	0.05		0.1	9.			
Trichlorofluoromethane					0.022	0.03	
Vinyl chloride	0.03						
Xylene			9.2				1.0

* Wet weight basis.
No. of samples = 1 or 2 (sample type not identified)

TRACE CONTAMINANT CHARACTERIZATION DATA

The concentrations of trace organic contaminants in four Wisconsin sludges are reported in Table 63. The most prevalent compounds were toluene, ethyl benzene and bis(2-ethylhexyl) phthalate. With the exception of two phthalate esters in Green Bay sludge, the contaminant concentrations were 2 ug/g or less.

TABLE 63. ORGANIC CONTAMINANT CONCENTRATIONS IN SELECTED WISCONSIN SLUDGES (KLEINERT, 1986)

COMPOUND	CONCENTRATION (ug/g)			
	MILWAUKEE SOUTH SHORE	RACINE	KENOSHA	GREEN BAY
Benzene	0.008			
Chlorobenzene			1.4	
Chloroform	0.003		0.57	
1,2-t-Dichloroethylene	0.009			
Ethylbenzene	0.43	0.0005	1.0	
Methylene Chloride	0.10			
Toluene	2.04	0.003	1.0	
Trichloroethylene	0.003			
Nitrobenzene		0.002		
Naphthalene	0.060			
1,4-Dichlorobenzene		0.002		
Bis(2-ethylhexyl)phthalate	0.034	0.004		8.8
Butylbenzyl phthalate				30.
Fluorene	0.009			
Phenanthrene	0.11			
Anthracene	0.147			
Di-n-butyl phthalate	0.044			
Acenaphthene	0.024			
Di-n-octyl phthalate	0.70			
Phenol	0.033			
alpha-Endosulfan		0.0001		
4,4'-DDD		0.00001		
delta-BHC			0.15	
Aldrin				0.150
Endrin				0.192
Hexachlorobenzene				0.012
No. of Samples	2 grabs	1 grab	1 grab	1 grab

The levels of trace organics detected in sludges from two Chicago treatment plants are summarized in Table 64. The data are reported on a wet weight basis and are not comparable to the results reported above. Toluene was the contaminant present at the highest concentration at the two plants. High levels of the PAH indeno(1,2,3-c,d)pyrene were found in both sludges, while benzo(a)pyrene was found at a substantial level in the Calumet plant sludge.

The concentrations of trace contaminants in combined primary and waste activated sludges from some of the plants initially investigated in the EPA 40 POTW study (EPA, 1982a) are reported on both wet and dry weight bases in Table 65 (Naylor and Loehr, 1982). For contaminants expressed on a dry weight basis, metals were present in the highest concentrations, particularly zinc, copper, lead and chromium. In the trace organics group, bis(2-ethylhexyl) phthalate, butylbenzyl phthalate and the purgeables chloroethane, toluene and trans-1,2-dichloroethylene were present at the highest levels (15-109 ug/g).

TRACE CONTAMINANT CHARACTERIZATION DATA

TABLE 64. CONTAMINANT CONCENTRATIONS IN TWO CHICAGO WASTEWATER TREATMENT PLANT SLUDGES (MSDGC, 1984)

COMPOUND	CONCENTRATION (ug/L)	
	CALUMET	WEST SOUTHWEST
Methylene chloride	<0.2	0.3
1,2-trans-Dichloroethylene	7.4	1.1
Benzene	5.7	1.4
Toluene	1291.	428.
Chlorobenzene	12.1	<1.
Ethyl benzene	35.0	8.0
Phenol	19.7	66.0
1,4-Dichlorobenzene	<0.5	36.0
Naphthalene	33.5	103.
Fluorene	15.8	27.0
Diethyl phthalate	<0.5	37.5
Phenanthrene	55.2	91.0
Anthracene	31.5	44.0
Di-n-butyl phthalate	21.7	<1.0
Fluoranthene	76.8	106.
Pyrene	88.6	75.0
Benzo(a)anthracene	51.0	53.0
Chrysene	63.0	75.0
Bis(2-ethylhexyl) phthalate	<0.5	128.
Benzo(b)fluoranthene	64.0	78.0
Benzo(k)fluoranthene	40.0	69.0
Benzo(a)pyrene	305.	<1.0
Indeno(1,2,3-c,d)pyrene	305.	259.
Dibenzo(a,h)anthracene	33.5	<1.0

Note: a) Solids concentrations in sludges were not specified

b) No. of samples or sample type not specified

TABLE 65. CONCENTRATIONS OF TRACE CONTAMINANTS IN MUNICIPAL SLUDGES (NAYLOR AND LOEHR, 1982)

CONTAMINANT	NO. TIMES DETECTED IN COMBINED SLUDGE	CONCENTRATION IN COMBINED SLUDGES			
		ug/L (wet)		ug/g (dry wt)	
		MEDIAN	RANGE	MEDIAN	RANGE
Bis(2-ethylhexyl)phthalate	13	3806	157-11257	109	4.1-273
Chloroethane	2	1259	517-2000	19	14.5-24
1,2-trans-dichloroethylene	11	744	42-54993	21	0.72-865
Toluene	12	722	54-26857	15	1.4-705
Butylbenzyl phthalate	11	577	1-17725	15	0.52-210
2-Chloronaphthalene	1	400	400	4.7	4.7
Hexachlorobutadiene	2	338	10-675	4.3	0.52-8
Phenanthrene	12	278	34-1565	7.4	0.89-44
Carbon tetrachloride	1	270	270	4.2	4.2
Vinyl chloride	3	250	145-3292	5.7	3-110
Dibenzo(a,h)anthracene	1	250	25	13	13
1,1,2-Trichloroethane	2	222	3-441	3.5	0.036-6.9
Anthracene	13	272	34-1565	7.6	0.89-44
Naphthalene	9	238	23-3100	7.5	.9-70
Ethylbenzene	12	248	45-2100	5.5	1.0-51
Di-n-butyl phthalate	12	184	10-1045	3.5	0.32-17
Phenol	11	123	27-4310	4.2	0.9-113
Methylene chloride	10	89	5-1055	2.5	0.06-30
Pyrene	12	125	10-734	2.5	0.33-18
Chrysene	9	85	15-750	2.0	0.25-13
Fluoranthene	10	90	10-600	1.8	0.35-7.1
Benzene	11	16	2-401	0.32	0.053-11.3
Tetrachloroethylene	11	14	1-1601	0.38	0.024-42
Trichloroethylene	10	57	2-1927	0.98	0.048-44
Cadmium				12	1.1-59
Chromium				278	63-1762
Copper				539	100-1427
Mercury				1.9	0.037-78
Nickel				86	12-803
Lead				300	39-1169
Zinc				1148	420-8468

TRACE CONTAMINANT CHARACTERIZATION DATA

Concentrations of contaminants in primary and secondary sludges from the Chattanooga treatment plant at which the EPA's 30 day study was conducted are summarized in Table 66. Almost all organic contaminant concentrations were higher in the primary sludge than the waste activated sludge. Some metal concentrations were higher in the waste activated sludge than the primary sludge when expressed on a dry weight basis. Metals were present in the highest concentrations of all contaminants in both primary and waste activated sludges. Trace organics present at high levels in the primary sludge were bis(2-ethylhexyl) phthalate (770 ug/L), naphthalene (538 ug/L), 1,2,4-trichlorobenzene (604 ug/L), toluene (515 ug/L) and phenol (223 ug/L).

In pilot plant studies investigating removal of purgeable contaminants, in both control and spiked trials, the primary sludges were found to have higher levels of purgeables than the secondary sludges (Petrasek et al, 1983a). In the primary sludges, compounds present in the highest concentrations during both control and spike trials were chlorobenzene, tetrachloroethylene plus tetrachloroethane, toluene and ethyl benzene. The data from this set of tests are reported in Table 67.

Concentrations of semi-volatile extractable compounds in sludges resulting from pilot plant activated sludge studies (both wet and dry weight concentrations) are reported in Table 68 (Petrasek et al, 1983b). Although the primary sludge was higher than the secondary sludge in extractable organic concentrations, when the levels are expressed on a dry weight basis, the pesticide/PCB group and phenols group had concentrations in the secondary sludge which exceeded those in the primary sludge. The PAH group was consistently present at higher levels in the primary sludge than in the secondary sludge, while the phthalate concentrations were generally higher in the primary sludge than in the secondary.

The accumulation of contaminants in sludges from various processes are summarized in Table 69 and are reported on a wet weight basis (Hannah et el, 1986). The primary sludge had higher levels of contaminants than either the waste activated sludge or trickling filter humus. The chemical sludge, generated by treatment of the wastewater with alum, contained levels that were equal to or greater than the concentrations found in the primary sludge. Metals, phthalate esters and PAH compounds were present in the highest levels in the sludges. Variability of the concentrations of contaminants in the sludge samples was often high, with standard deviations frequently ranging from 50 to 80 percent of the mean levels.

The concentrations of trace contaminants in sludges from 74 treatment plants in Missouri, are summarized in Table 70 (Clevenger et al, 1983). Trace metals, particularly zinc, chromium and copper, were present in the highest levels (up to 1800 ug/g dry weight). Of the pesticides and PCBs reported, chlordane and PCBs had the highest concentrations.

A total of 444 sludges in the United Kingdom were analyzed for organochlorine insecticides and PCBs (McIntyre and Lester, 1984). The results, reported in Table 71, are expressed on a dry weight basis. Mean concentrations ranged from 0.03 ug/g for aldrin to 0.50 for dieldrin. The variability of the concentrations was extremely large with RSD values ranging from 100 percent for Aldrin to 873 percent for Lindane. Although all sludge types (i.e. primary, combined primary and secondary,

TRACE CONTAMINANT CHARACTERIZATION DATA

TABLE 66. CONCENTRATIONS OF CONTAMINANTS IN SLUDGES DURING 30-d STUDY (EPA, 1982b)

CONTAMINANT GROUP	CONTAMINANT	PRIMARY SLUDGE		SECONDARY SLUDGE	
		WET CONC. (ug/L)	DRY CONC. (ug/g)	WET CONC. (ug/L)	DRY CONC. (ug/g)
Volatiles	Benzene	13	0.57	2	0.3
	1,2-Dichloroethane	4	0.2	ND	ND
	1,1,1-Trichloroethane	96	4.2	4	0.5
	1,1-Dichloroethane	7	0.3	ND	ND
	1,1,2-Trichloroethane	63	2.8	<1	2.5
	Chloroform	69	3.0	18	2.5
	Ethylbenzene	63	2.8	9	1.0
	Methyiune chloride	21	0.9	33	4.5
	Tetrachloroethylene	51	2.2	10	1.4
	Toluene	515	22.6	86	12
	Trichlorotehylene	157	6.9	4	0.5
Acid Extract	4-Nitrophenol	ND	ND	13	1.8
	Pentachlorophenol	ND	ND	5	0.7
	Phenol	223	9.8	ND	ND
Base-Neutrals	Acenaphthene	16	0.70	ND	ND
	1,2,4-Trichlorobenzene	604	26.5	115	15.7
	Hexachloroethane	2	0.09	ND	ND
	1,2-Dichlorobenzene	63	2.8	2	0.3
	1,4-Dichlorobenzene	41	1.8	ND	ND
	2,6-Dinitrotoluene	2	0.09	ND	ND
	Fluoranthene	196	8.6	17	2.3
	4-Chlorophenyl phenyl ether	4	0.2	ND	ND
	Naphthalene	538	23.6	46	6.3
	Bis(2-ethylhexyl) phthalate	770	33.8	180	24.6
	Butylbenzyl phthalate	24	1.1	33	4.5
	Di-n-butyl phthalate	ND	ND	11	1.5
	D-n-octyl phthalate	5	0.2	ND	ND
	Diethyl phthalate	37	1.6	ND	ND
	1,2-Benzofluoranthene	37	1.6	4	0.5
	Benzo(a)pyrene	31	1.4	ND	ND
	11,12-Benzofluoranthene	31	1.4	1	0.1
	Chrysene	44	1.9	4	0.5
	Acenaphthylene	5	0.2	2	0.3
	Anthracene	47	2.1	1	0.1
	Fluorene	55	2.4	ND	ND
	Phenanthrene	157	6.9	1	0.1
	Indeno(1,2,3-c,d)pyrene	5	0.2	ND	ND
	Pyrene	108	4.73	6	0.8
Pesticides	alpha-BHC	0.003	.001	ND	ND
Metals	Antimony	91	4.0	19	2.6
	Arsenic	750	32.9	139	19.0
	Beryllium	67	2.9	23	3.1
	Cadmium	193	8.5	76	10
	Chromium	14760	647	6417	877
	Copper	7110	312	1380	189
	Cyanide	1010	44.3	183	25
	Lead	4509	198	787	108
	Mercury	34	1.5	1.2	0.16
	Nickel	4388	192	823	113
	Selenium	7	0.3	<40	<5
	Silver	577	25.3	206	28.1
	Zinc	25889	1135	3934	538

ND = Not Detected

TABLE 67. ACCUMULATION OF PURGEABLE CONTAMINANTS IN WASTEWATER SLUDGES
(PETRASEK ET AL, 1983a)

COMPOUND	CONTROL RUNS			SPIKED RUN		
	INFLUENT (ug/L)	PRIMARY SLUDGE (ug/L)	RETURN ACTIVATED SLUDGE (ug/L)	INFLUENT (ug/L)	PRIMARY SLUDGE (ug/L)	RETURN ACTIVATED SLUDGE (ug/L)
Methylene chloride	<30.6	<40.4	<1.4	118	<143	<21
1,1-Dichloroethene	<10.7	bdl*	bdl	79	<40	<1
Chloroform	10.8	<7.5	<3.4	137	<208	<7
Carbon tetrachloride	<6.2	<1.5	bdl	60	<14	<1
1,2-Dichloropropane	<0.2	<3.6	<1.2	309	<461	<1
Trichloroethylene	<4.2	<23.3	bdl	107	389	<1
1,1,2-Trichloroethane	<2.9	<3.2	<6.5	133	<219	31
Dibromochloromethane	<0.6	bdl	<1.3	58	<10	<2
Benzene	<2.7	<9.0	<1.5	73	121	<1
1,1,1-Trichloroethane	<65.0	<37.2	<1.5	132	<220	<1
Bromodichloromethane	<0.2	bdl	bdl	89	<25	<1
Chlorobenzene	102	648	<1.6	197	953	<5
Tetrachloroethylene & Tetrachloroethane	<24.0	164	<3.0	252	2033	25
Toluene	160	654	NR**	255	974	<2
Ethylbenzene	<24.5	283	bdl	82	766	<1

* bdl = Below Detection Limit

** NR = Not Reported

No. of grab samples = 20

TABLE 68. ACCUMULATION OF SEMI-VOLATILE EXTRACTABLE COMPOUNDS BY WASTEWATER SLUDGES (PETRASEK *ET AL*, 1983b)

COMPOUND	INFLUENT (ug/L)	PRIMARY SLUDGE (ug/L)	RETURN ACTIVATED SLUDGE (ug/L)	PRIMARY SLUDGE (ug/g)	RETURN ACTIVATED SLUDGE (ug/g)
Pesticides/PCBs					
Aroclor 1254	<33.5	13,500	5403	165.0	844.0
Heptachlor	31.7	<2,152	526	16.0	82.0
Lindane	45.5	<1,130	<173	5.3	27.0
Toxaphene	<47.4	<8,213	<1655	51.0	259.0
Phenols					
2,4-Dimethylphenol	95.7	<20	<20	0.6	3.1
Phenol	261.3	<2,348	<92	2.8	14.0
Pentachlorophenol	7.6	<410	<20	0.6	3.1
Phthalates					
Bis(2-ethylhexyl) phthalate	51.7	6,713	978	205.0	153.0
Butylbenzyl phthalate	33.5	<8,160	<123	250.0	19.0
Diethyl phthalate	46.4	<710	<196	22.0	31.0
Dimethyl phthalate	47.3	<37	<39	1.1	6.2
Di-n-butyl phthalate	43.8	3,482	<233	107.0	37.0
Di-n-octyl phthalate	28.2	<5,278	<580	162.0	91.0
Polynuclear Aromatic Hydrocarbons					
Acenaphthene	39.8	3,354	<68	103.0	11.0
Anthracene	34.8	4,809	<84	147.0	13.0
Benzo(a)anthracene	23.8	<3,241	<208	99.0	33.0
Chrysene	38.9	5,982	<240	183.0	38.0
Fluoranthene	30.6	5,281	<196	162.0	31.0
Fluorene	37.9	<3,921	<57	120.0	9.0
Naphthalene	76.7	<3,463	<18	106.0	2.9
Phenanthrene	40.4	<4,931	<28	151.0	4.4
Pyrene	30.4	<6,640	<104	203.0	16.0

No. of samples = 8 24-hr composites

TABLE 69. CONCENTRATIONS OF TRACE CONTAMINANTS IN WASTEWATER PROCESS SLUDGES
(HANNAH ET AL, 1986)

COMPOUND	CONTAMINANT CONCENTRATION (ug/L)									
	WASTEWATER FEED		PRIMARY SLUDGE		WASTE ACTIVATED SLUDGE		TRICKLING FILTER SLUDGE		CHEMICAL SLUDGE	
	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ
Carbon Tetrachloride	69	33	20	10	14	4	12	5	14	4
1,1-Dichloroethane	144	24	135	30	9	2	60	32	139	14
1,1-Dichloroethylene	212	72	156	38	13	12	47	38	181	63
Chloroform	135	16	126	35	12	4	60	42	149	30
1,2-Dichloroethane	153	44	128	25	24	19	77	30	127	59
Bromoform	90	35	27	13	18	4	15	4	25	16
Ethylbenzene	111	21	312	150	3	1	28	16	511	393
Bis(2-ethylhexyl) phthalates	168	74	5550	3450	4350	3630	1425	860	9900	5850
Dibutyl phthalate	73	26	1150	850	284	474	356	157	3100	2050
Naphthalene	108	34	620	490	29	26	230	66	1180	715
Phenanthrene	95	24	2850	2010	184	165	820	304	5925	3425
Pyrene	104	18	4000	2750	366	254	1140	620	8550	4575
Fluoranthene	104	19	4000	2950	337	226	1040	525	8250	4350
Isophorone	89	30	70	34	19	6	106	52	84	76
Bis(2-chloroethyl)ether	143	51	129	81	115	68	262	115	152	62
p-Dichlorobenzene	93	17	580	515	36	17	169	80	1150	740
Phenol	126	49	465	545	565	780	395	291	358	257
2,4-Dichlorophenol	228	178	199	102	ND	ND	483	225	464	569
Pentachlorophenol	84	46	119	69	110	131	174	145	1175	1260
Lindane (gamma-BHC)	39	6	1010	640	204	69	240	148	707	127
Heptachlor	39	3	1180	208	658	201	383	116	1967	208
Chromium	221	88	15600	6900	12800	13600	5600	4600		
Copper	345	119	23500	9200	14900	12600	7000	4800		
Nickel	141	93	5200	2900	3500	2800	2000	1600		
Lead	165	168	10100	4600	5300	4600	2700	2400		
Cadmium	25	23	600	500	400	500	200	100		

Samples were manually composited into a daily composite sample.

No. of samples not specified

$\bar{x}$ = Mean concentration

σ = Standard deviation of mean

TABLE 70. CONCENTRATIONS OF TRACE CONTAMINANTS IN SLUDGES FROM 74 MISSOURI MUNICIPALITIES (CLEVENGER _ET AL_, 1983)

COMPOUND	CONCENTRATION (ug/g dry wt.)			
	MINIMUM	MAXIMUM	MEAN	MEDIAN
PCB	0.11	2.9	1.1	0.99
Lindane	0.05	0.22	0.11	0.11
Chlordane	0.46	12	3.2	2.75
Aldrin	0.05	0.64	0.13	0.08
Heptachlor epoxide	0.05	0.55	0.15	0.13
DDE	All samples below Detection Limit (<0.05)			
Dieldrin	0.05	0.81	0.14	0.11
Endrin	0.11	0.17	0.14	0.14
DDT	0.06	0.14	0.10	0.09
BHC	All samples below Detection Limit (<0.02)			
Arsenic	2	39	7.5	6.1
Cadmium	1.7	320	22	8.1
Chromium	10	12000	660	85.5
Copper	45	5200	550	390
Mercury	0.6	130	7.7	3.9
Nickel	10	13000	330	33.5
Lead	42	960	210	145
Zinc	170	13000	1800	1200

No. of samples = 3 to 4 in each of 74 municipalities
Sample type not specified

TABLE 71. CONCENTRATIONS OF ORGANOCHLORINE INSECTICIDES IN UNITED KINGDOM SLUDGES (McINTYRE AND LESTER, 1984)

COMPOUND	MEAN CONCENTRATION (ug/g)	STANDARD DEVIATION (ug/g)	RELATIVE STANDARD DEVIATION (%)
PCB	0.34	1.23	362
gamma-BHC (Lindane)	0.41	3.58	873
Aldrin	0.03	0.03	100
Dieldrin	0.50	3.07	614
Endrin	0.11	0.16	145

No. of grab samples = 444

digested) were classed together for calculation of the mean concentrations, testing by analysis of variance indicated that the variability in concentrations was not due to sludge type.

There is reasonable agreement between the mean concentrations of pesticides/PCBs reported for Missouri sludges by Clevenger _et al_ (1983) and McIntyre and Lester (1984).

3.4.2 Internal Recycle Streams

The concentrations of trace contaminants in raw sludge subjected to heat treatment are reported in Table 72 (Nicholls *et al*, 1979). In general, less than 10 percent of the metals in the sludge were resolubilized by heat treatment, and PAHs were essentially unaffected by heat treatment.

TABLE 72. CONCENTRATIONS OF TRACE CONTAMINANTS IN RAW SLUDGE AND HEAT TREATED SLUDGE STREAMS (NICHOLLS *ET AL*, 1979)

CONTAMINANT	CONCENTRATION RANGE (ug/g)		
	RAW SLUDGE	PRESS/DECANT LIQUORS	SLUDGE CAKE
Cadmium	16 - 75	<0.2 - 30	15 - 63
Chromium	360 - 1400	62 - 330	370 - 1500
Copper	310 - 480	<2 - 86	340 - 540
Nickel	33 - 220	16 - 64	34 - 230
Lead	280 - 530	<2 - 185	315 - 560
Zinc	560 - 1800	5 - 325	640 - 2000
Fluoranthene	0.525 - 1.20	0.04 - 1.50	0.47 - 1.60
Benzo(b)fluoranthene	0.21 - 0.42	0.03 - 0.55	0.31 - 0.52
Benzo(k)fluoranthene	0.10 - 0.42	0.03 - 0.45	0.09 - 0.33
Benzo(a)pyrene	0.27 - 0.57	0.03 - 0.84	0.31 - 0.52
Benzo(g,h,i)perylene	0.10 - 0.29	0.01 - 0.50	0.09 - 0.44
indeno(1,2,3-cd)pyrene	0.21 - 0.42	0.03 - 0.55	0.22 - 0.57

The effects of three sludge processing methods on the concentrations of contaminants in raw sludge were investigated by CANVIRO Consultants Ltd. (1984b). The three processes included heat treatment, anaerobic digestion and anaerobic digestion plus polymer addition. Seven trace organic compounds (PAHs) and six trace metals were observed in the study. Heat treatment was found to reduce the total mass of organics in the sludge, but resulted in increased levels in the soluble fraction, contrary to the observations of Nicholls *et al* (1979). Anaerobic digestion resulted in higher levels of soluble organics than in either the untreated sludge or heat treated sludge. Digestion with polymer addition reduced the levels of soluble trace organics. Heat treatment significantly increased soluble metal concentrations, with increases of 85 percent for copper up to 700 percent for nickel. Only lead was decreased in concentration in the soluble fraction. Although anaerobic digestion alone did not affect the soluble fraction of metals in the sludge, digestion with polymer addition resulted in lower concentrations of soluble metals.

Two plants in the 40 POTW study (EPA, 1982a) used heat treatment for processing sludge. In one plant (#7 in Table 73), it appeared as though much of the organics in the feed sludge were reduced by heat treatment, in agreement with the observations of CANVIRO (1984b). Only benzene, toluene, phenol, 1,3-dichloropropylene and 1,2-dichloropropane had higher levels in the heat treated sludge than in the feed. Metal concentrations were also higher in the combined sludge at Plant #7 than in the heat treated sludge. Mass balances around the heat treatment unit indicated that the metals could generally be accounted for, but the mass of organics in the heat treated sludge and decant liquor was usually substantially less than in the combined sludge. Destruction of most organics was indicated.

TABLE 73. COMPARISON OF CONTAMINANT CONCENTRATIONS BEFORE AND AFTER HEAT TREATMENT OF SLUDGE (EPA, 1982b)

CONTAMINANT GROUP	CONTAMINANT	PLANT #7		PLANT #8	
		COMBINED SLUDGE (ug/L)	HEAT TRT SLUDGE (ug/L)	COMBINED SLUDGE (ug/L)	HEAT TRT SLUDGE (ug/L)
Volatiles	Acrylonitrile	ND	ND	25	165
	Benzene	95	507	16	773
	Chlorobenzene	6	1	<5	33
	1,1,1-Trichloroethane	ND	ND	<5	13
	1,1-Dichloroethane	352	ND	1	<5
	1,1,2-Trichloroethane	ND	ND	3	<5
	1,1,2,2-tetrachloroethane	26	ND	<5	13
	Chloroethane	ND	ND	2000	<5
	Chloroform	7	ND	<5	<5
	1,1-Dichloroethylene	ND	ND	<5	5
	1,2-trans-Dichloroethylene	1517	283	1259	805
	1,2-Dichloropropane	ND	8	2	3
	Ethylbenzene	2100	460	359	1266
	Methylene Chloride	8	1	<5	<5
	Methyl Bromide	ND	ND	<5	125
	Dichlorodifluoromethane	ND	ND	<5	5
	Tetrachloroethylene	32	ND	494	1893
	Toluene	1	15	3	240
	Trichloroethylene	4615	2343	7635	41575
	Vinyl Chloride	2	7	5	185
	1,2-Dichlorobenzene	ND	ND	250	<5
Acids	2,4-Dichlorophenol	ND	ND	ND	ND
	Pentachlorophenol	1000	ND	823	1300
	Phenol	173	1717	610	1238
Base-Neutrals	Acenaphthene	ND	ND	1150	ND
	Hexachlorobenzene	ND	ND	195	ND
	2-Chloronaphthalene	ND	ND	400	ND
	1,2-Dichlorobenzene	233	50	258	ND
	1,3-Dichlorobenzene	35	ND	275	ND
	1,4-Dichlorobenzene	28	10	325	ND
	Fluoranthene	143	13	600	577
	Hexachlorobutadiene	ND	ND	675	ND
	Naphthalene	180	16	1159	686
	Bis(2-ethylhexyl)Phthalate	11257	10117	10500	20200
	Butyl Benzyl Phthalate	1162	735	17775	33425
	Di-n-butyl Phthalate	318	265	1045	1688
	Diethyl Phthalate	ND	ND	ND	ND
	Dimethyl Phthalate	ND	ND	160	ND
	1,2-Benzanthracene	153	25	750	119
	Benzo(a)pyrene	ND	ND	ND	11
	Chrysene	153	25	750	119
	Anthracene	827	407	1565	690
	Phenanthrene	827	407	1565	690
	Pyrene	160	14	734	768
Metals	Antimony	1403	1047	1015	1825
	Arsenic	332	207	695	1463
	Beryllium	<10	<10	22	44
	Cadmium	498	313	450	780
	Chromium	72667	56000	101250	150000
	Copper	45833	35333	120500	202500
	Cyanide	2503	278	3040	1526
	Lead	44167	6133	98750	95250
	Mercury	205.0	140.5	172.5	505.0
	Nickel	27333	20667	60000	92000
	Selenium	153	93	170	328
	Silver	177	85	160	160
	Zinc	128333	98833	71500	1335000

No. of composite samples = 6 for Plant 7
= 3-4 for Plant 8

At Plant #8 in Table 73, many of the purgeables and phthalates were higher in concentration after heat treatment than before. The solids levels in feed and heat treated sludge were 8.4 percent and 19.5 percent, respectively. The data indicated that compounds such as the phthalates remained relatively constant on a dry weight basis after heat treatment, while some purgeables such as benzene and toluene increased due to the process. Conversely, most of the PAH group were reduced by the treatment in Plant #8. At both plants, cyanide concentrations were significantly reduced by heat treatment.

In the 40 plant study by the EPA (1982a), the heat treatment decant liquor from two plants was characterized. The concentrations of the contaminants are summarized in Table 74. The concentrations of contaminants in the heat treatment liquors are considerably different reflecting the different sludge origins. In Plant #7, bis(2-ethylhexyl) phthalate, copper and lead displayed high concentrations, while at Plant #8, the waste stream had a high concentration of toluene. The solids levels of the two streams were approximately equal at 1.0 to 1.4 percent.

Digester supernatant at the Chattanooga treatment plant which was involved in the 30 day study (EPA, 1982b) was characterized with the average concentrations reported in Table 74. Other than the metals zinc, chromium, copper, lead and nickel, contaminants present at high concentrations were ethyl benzene (269 ug/L) and toluene (146 ug/L).

Metal concentrations in waste activated sludge, combined sludge, Zimpro (wet air oxidation) recycle stream and filter press cake at the Lansing, MI wastewater treatment plant are reported in Table 75 (Kang *et al*, 1981). Both the waste activated sludge and the blended sludge had high levels of all metals investigated. Copper and zinc in the combined sludge at 102,000 and 125,000 ug/L were present in particularly high levels. The wet air oxidation recycle stream also had high metal concentrations, ranging from 5,440 ug/L for nickel to 27,300 ug/L for zinc. The filter cake had correspondingly high levels of metals as well.

The concentrations of trace contaminants in two vacuum filter filtrates are reported in Table 74 (EPA, 1982a; 1982b). At Plant 26 of the 40 plant study, the vacuum filter treats combined primary and secondary sludge wasted from the primary clarifiers. Metals and cyanide had the highest concentrations (up to 4782 ug/L for zinc); only bis(2-ethylhexyl)phthalate was observed above 100 ug/L in the organic compounds, with the balance found at less than 50 ug/L. The vacuum filtrate at the Chattanooga, TN plant used in the 30 day study (EPA, 1982b) also had very low levels of trace organics (14 ug/L or lower). Zinc and chromium, at 340 and 130 ug/L, respectively, were the only metals above 100 ug/L.

At the Hamilton, Ontario WPCP, the in-plant recycle stream consists of waste activated sludge, digester supernatant, vacuum filter filtrate, incinerator ash quench water , miscellaneous clean-up waters, and periodic discharges resulting from digester cleanout or aeration basin emptying (Zukovs *et al*, 1984). The in-plant recycle stream was sampled to evaluate the loading of trace contaminants contributed by the in-plant recycle stream to the total combined influent. The results are summarized in Table 76. The recycle stream contributed to 21 to 25 percent of metals, with the exception of nickel, to the combined influent. The in-plant recycle contribution of organics

TRACE CONTAMINANT CHARACTERIZATION DATA

TABLE 74. CONCENTRATIONS OF TRACE CONTAMINANTS IN POTW SIDE STREAMS (EPA, 1982a)

CONTAMINANT	HEAT TREATMENT DECANT LIQUOR		VACUUM FILTER FILTRATE	DIGESTER SUPERNATANT	VACUUM FILTER FILTRATE
	PLANT #7 (ug/L)	PLANT #8 (ug/L)	PLANT #26 (ug/L)	(EPA, 1982b) (ug/L)	(EPA, 1982b) (ug/L)
Benzene	22	22	1	10	2
1,2-t-Dichloroethylene	9	<2	22	18	<1
Ethylbenzene	18	7	28	269	2
Methylene Chloride	38	19	2	15	12
Toluene	63	1825	32	146	8
Chlorobenzene	<1	1	1	37	<1
Trichloroethylene	<5	2	27	<1	<1
1,1-Dichloroethane				3	ND
1,1,1-Trichloroethane	<5	<2	1	<1	<1
Chlorofrom	<5	<1	1	<1	<1
Tetrachloroethylene	<5	<2	25	<2	<2
Phenol	907	334	39	17	14
Pentachlorophenol	<250	60	1	<1	<1
2,4-Dichlorophenol	ND	2	<1	<1	<1
2,4-Dimethylphenol	ND	<2	1	<1	4
1,2-Dichlorobenzene	17	<2	<20	<1	<1
Naphthalene	2	2	44	41	12
Bis(2-ethylhexyl) phthalate	1498	6	140	49	14
2-Chloronaphthalene	ND	<3	1		
1,2,4-Trichlorobenzene	ND	ND	ND	7	<1
1,3-Dichlorobenzene	<100	<2	<25	25	2
1,4-Dichlorobenzene	<100	<2	<25	4	<1
1,4-Diphenylhydrazine	ND	ND	ND	1	2
Bis(2-chloroethoxyl) methane	ND	ND	ND	2	<1
Nitrobenzene	ND	ND	ND	5	<1
N-Nitrosodiphenylamine	ND	ND	ND	4	<1
Di-n-butylphthalate	<100	<3	<20	5	1
Di-n-octylphthalate	ND	ND	<25	9	4
Diethylphthalate	<100	<4	ND	9	11
Acenaphthene	ND	<10	ND	1	<1
Fluoranthene	<50	<3	<20	4	<1
Benzo(a)anthracene	<50	<3	ND	1	<1
Acenaphthylene	ND	ND	ND	<1	5
Anthracene	<100	<3	<25	6	2
Aldrin	ND		0.030	ND	ND
Heptachlor	0.333	ND	1.563	ND	ND
Heptachlor Epoxide	0.083	ND	0.283	ND	ND
gamma-BHC	0.167	ND	0.057	ND	ND
Antimony	54	<500	<50	2	<10
Arsenic	56	<500	23	32	5
Cadmium	139	<2	58	11	<5
Chromium	9569	1155	729	512	130
Copper	5701	212	1480	340	94
Lead	1701	192	982	262	41
Mercury	1.0	0.23	2.48	2.46	0.64
Nickel	9888	6945	248	212	51
Silver	27	<2	100	14	4
Zinc	32602	7495	4782	1184	340
Cyanide	49	44	786	33	12
No. of Samples	6 composite	4 composite	6 composite	5 grab	5 grab

TABLE 75. METAL CONCENTRATIONS IN SLUDGE PROCESSING STREAMS AT A MICHIGAN WASTEWATER TREATMENT PLANT (KANG ET AL, 1981)

METAL	SLUDGE STREAM			
	WASTE ACTIVATED (ug/L)	COMBINED (ug/L)	ZIMPRO RECYCLE (ug/L)	FILTER CAKE (ug/g)
Cadmium	60	460	60	15.9
Chromium	7900	49500	6440	1460
Copper	18300	102000	14000	3340
Lead	8200	55100	7140	1840
Nickel	3800	25900	5440	621
Zinc	16900	125000	27300	3300

No. and type of samples not specified

TABLE 76. CONTRIBUTION OF TRACE CONTAMINANTS IN HAMILTON (ONTARIO) IN-PLANT RECYCLE STREAM TO TOTAL COMBINED INFLUENT (ZUKOVS ET AL, 1984)

CONTAMINANT	TOTAL IN-PLANT RECYCLE AS PERCENT OF COMBINED INFLUENT MASS LOAD
Chromium	23
Copper	22
Nickel	12
Lead	25
Zinc	21
Naphthalene	6
Acenaphthalene	9
Dibenzofuran	11
Fluorene	18
Fluoranthene	39
Carbazole	11
Pyrene	52
Benzo(a)pyrene	18

to the combined influent was more variable, ranging from 6 percent for naphthalene to 52 percent for pyrene. No analysis was performed for purgeable or acid-extractable compounds. The study indicated that return streams could constitute a substantial loading of trace contaminants in total combined influent at a WPCP.

Summary of Sludge and Internal Recycle Stream Contaminant Data

Metals are the contaminants which occur most frequently in wastewater treatment plant sludges, and are present in the highest concentration. Zinc, copper and chromium are the predominant metals. Organic contaminants which occur regularly in sludge include phthalate esters, certain PAHs, toluene, ethyl benzene and tetrachloroethylene. Sludges from certain municipalities have high levels of other specific compounds.

Contaminant concentrations appear to be a function of the solids concentration, and hence, when contaminant levels are being compared, expression of the concentrations on a dry weight basis provides the most meaningful basis for comparison from various sources.

The data reviewed indicate that PAHs, phthalates and some purgeables (toluene, ethyl benzene, chlorobenzene, tetrachloroethylene) are present at higher levels (dry weight basis) in primary sludge than secondary sludge, whereas the reverse is observed for pesticides and phenolic compounds.

The data characterizing other wastewater treatment process side streams are generally scarce. The limited data indicate that different side streams could cause high loadings to the treatment plant when returned (e.g. digester supernatant, heat treat liquor), especially with respect to metals and phthalate esters. Although some purgeables may be returned at elevated levels, it is probable that the secondary section of the treatment plant would be capable of removing them, based on the work of Jones (1984), especially if the side stream is returned on a continuous basis. Some side streams (e.g. vacuum filter filtrate) should have less impact on trace contaminants returned to the plant.

From the data reviewed on sludge processing by heat treatment, it appears that some contaminants are reduced in concentration (e.g. PAHs, cyanide, some purgeables and phenolics), while others are relatively unaffected (metals, phthalate esters). Heat treatment may increase some compounds (benzene, toluene, phenol), as breakdown products of more complex organic contaminants. Assessment of the efficiency of the process is best done on a dry weight basis. The importance of the soluble fraction of contaminants to overall concentrations should not be overlooked, because the process may result in significant solubilization of certain pollutants. Similarly, anaerobic digestion may result in higher levels of soluble organic compounds, but not metals.

4.0 REMOVAL OF TRACE CONTAMINANTS IN WASTEWATER TREATMENT PLANTS

4.1 Removal of Trace Contaminants by Full-Scale Treatment Plants

Comparison of removal efficiencies is difficult because the calculated removals may be based upon concentrations in non-chlorinated or chlorinated effluent samples. Chlorinated effluents often have elevated concentrations of certain compounds such as chloroform and methylene chloride, and removal efficiences in these cases are frequently zero or negative. Because of the manner in which the data were reported, it is often impossible to determine whether the trace organic analyses were performed in chlorinated or non-chlorinated effluent samples.

The removal efficiencies of trace contaminants by four Metro Toronto water pollution control plants are summarized in Table 77. In the purgeables category, compounds such as the xylenes and ethyl benzene had high removals. Chloroform was poorly removed. With respect to acid extractable compounds, phenol and p-cresol were removed to a high degree, while pentachlorophenol and 2,4-dimethylphenol generally had low removals. The North Toronto plant did reduce the 2,4-dimethylphenol raw wastewater concentration by 84 percent. In the base-neutral extractable group, phthalates were typically reduced by 70 percent or higher. Anthracene, a PAH, was poorly removed. Pesticide removals were inconsistent in the four plants.

Removals of trace contaminants by three Niagara (Ontario) area water pollution control plants are summarized in Table 78. The Welland treatment plant, which is an activated sludge plant, typically had higher metals removals than Fort Erie or Niagara Falls, which are primary treatment plants. Removal efficiencies for cadmium, nickel and cyanide were poor for the three plants. Removals of purgeable compounds and pesticides were quite variable, and in a number of cases, negative removals of compounds were noted for all 3 plants (e.g. benzene, ethyl benzene, o-xylene and alpha-BHC). The high number of cases in which the removals could not be determined, or in which negative removals were achieved, is a consequence of the number of concentrations at or below the detection limit.

Removals of inorganic contaminants by Ohio wastewater treatment plants are reported in Table 79. Copper was removed most consistently at high efficiency in all the plants. Metal removals were generally higher for Wapakoneta and Dayton than for the other treatment plants and these two plants had the highest concentrations of inorganics in the raw wastewaters in this group of Ohio treatment plants. For most metals, higher removal efficiencies are associated with higher influent concentrations.

Organic contaminant removal efficiencies in selected Ohio treatment plants are summarized in Table 80. Contaminant removal efficiencies are variable due in part to raw wastewater concentrations near the detection limits and detection limits which varied from one plant to another. Contaminants such as trichloroethylene, tetrachloroethylene and methylene chloride were typically removed at high efficiencies. It is not clear from the data provided if the effluents were chlorinated or not.

TABLE 77. REMOVAL OF TRACE ORGANIC CONTAMINANTS BY METRO TORONTO WPCPs

COMPOUNDS	REMOVAL (%)			
	TORONTO MAIN	NORTH TORONTO	HIGHLAND CREEK	HUMBER
Purgeable				
1,1-Dichloroethylene	>40		>85	>65
Dichloromethane	62	64	Increase	69
1,1-Dichloroethane	>89			
Chloroform	Increase	12	Increase	31
1,1,1-Trichloroethane	>72		94	94
Trichloroethylene	>23		>50	>42
Toluene	>99	>52	>95	>52
Tetrachloroethylene	>70		Increase	>46
Ethyl benzene	>92		>88	>94
P- and m-Xylene	>95	>44	>94	>91
o-Xylene	>96	>21	>90	>90
1,4-Dichlorobenzene	54		>64	65
1,2-Dichlorobenzene	>64	>20		>64
Acid Extractable				
Phenol	99	95	98	98
2,4-Dimethylphenol	Increase	84	10	Increase
p-Chloro-m-cresol	CBD	>19	-	>82
Pentachlorophenol	58	21	Increase	-
p-Cresol	>78	>56	>38	81
m-Cresol	>78	>56	>34	99.5
p-Cresol	>99	>96	>99.7	>99
B/N Extractable				
1,4-Dichlorobenzene	54	77	37	65
1,2-Dichlorobenzene	77	87	0	58
Naphthalene	91	>33	>50	91
Diethyl phthalate	94	80	97	94
Phenanthrene	>17	-	-	CBD
Anthracene	0	Increase	-	Increase
Di-n-butyl phthalate	89	Increase	94	64
Bis(2-ethylhexyl) phthalate	72	78	59.4	80
Pesticide				
Hexachlorobenzene	Increase		50	Increase
alpha-BHC		80		
beta-3HC		>90		
gamma-BHC	71	Increase	55	0
4,4,'-DDD		38		
4,4'-DDE	Increase	90		
Dieldrin	Increase			
alpha-Endosulfan		Increase		
Oxychlordane		Increase		
Atrazine	Increase			Increase
2,4-D	>52	>41	-	

CBD = Cannot be determined from data

Increase = Eff. conc. > Inf. conc.

TABLE 78. REMOVALS OF TRACE ORGANIC CONTAMINANTS BY NIAGARA REGION WPCPs

CONTAMINANTS	REMOVAL (%)		
	WELLAND	FORT ERIE	NIAGARA FALLS
Inorganic			
Arsenic	0%	CBD	CBD
Cadmium	Increase	Increase	
Chromium	75	25	83
Copper	80	33	34
Mercury (ug/L)	74	65	73
Nickel	Increase	Increase	17
Lead	41	60	25
Zinc	84	29	69
Cyanide	Increase	Increase	60
Dichloromethane	Increase	92	94
Chloroform	Increase	Increase	52
1,1,1-Trichloroethane	30	10	Increase
1,1,2-Trichloroethane	>33	94	
Bis-1,2-Dichloroethylene	CBD	67	
Trichloroethylene	20	Increase	Increase
Tetrachloroethylene	Increase	Increase	64
Benzene	Increase	Increase	Increase
1,2-Dichlorobenzene	65	Increase	Increase
1,3-Dichlorobenzene	Increase	0	Increase
1,4-Dichlorobenzene		50	Increase
Ethyl benzene	Increase	Increase	Increase
Toluene	67	17	Increase
Chlorotoluenetrifluoride	98		
o-Xylene	Increase	Increase	Increase
m-Xylene	Increase	26	Increase
p-Xylene	>67	0	20
Chlorodibromomethane	CBD	CBD	>80
Dichlorobromomethane	CBD	CBD	>73
1,1-Dichloroethane	CBD	99.9	CBD
1,2-Dichloroethane	CBD	Increase	Increase
Chloromethane		CBD	-
Bromoform		20	
1,1-Dichloroethylene		Increase	Increase
1,2-t-Dichloroethylene		Increase	Increase
1,3-t-Dichloropropylene		Increase	
Chlorobenzene		0	Increase
alpha-BHC	Increase	Increase	Increase
gamma-BHC	5	34	Increase
alpha-Chordane	Increase	1	CBD
gamma-Chlordane	Increase	0	CBD
Dieldrin	CBD	54	
Hexachlorobenzene	76		29
beta-BHC	Increase		
p,p-DDE		CBD	80
Aroclor 1254		22	>50
Methoxychlor			Increase
Endosulfan I			Increase

CBD = Cannot be determined

Increase = Eff. conc. > Inf. conc.

TABLE 79. TRACE METALS REMOVALS BY SELECTED OHIO WASTEWATER TREATMENT PLANTS (BULZAN, 1986)

INORGANIC	REMOVAL (%)				
	MARION	ALLIANCE	LIMA	WAPAKONETA	DAYTON
Arsenic	>20	-	-	-	>60
Cadmium	0	-	Increase	50	-
Chromium	-	>33	Increase	92	74
Copper	76	78	>60	76	79
Mercury	-	-	Increase	-	-
Nickel	-	-	39	60	Increase
Lead	-	-	>61	91	-
Zinc	3	60	44	55	59
Cyanide	34	-	80	-	40

Increase = Eff. conc. > Inf. conc.

TABLE 80. REMOVAL OF ORGANIC CONTAMINANTS BY SELECTED OHIO WASTEWATER TREATMENT PLANTS (BULZAN, 1986)

CONTAMINANT	REMOVAL (%)						
	WAPAKONETA	LIMA	TOLEDO	DAYTON	ALLIANCE	COLUMBUS JACKSON PIKE	COLUMBUS SOUTHERLY
1,1,1-Trichloroethane	76	Increase		>88.9			
1,1,2,2-Trichloroethane							
1,2-Diphenylidrazine							
1,2-t-Dichloroethylene	>54.5			>85.4			>47.4
1,4-Dichlorobenzene	>9.1						
4-Methyl phenol				>56.5			
Anthracene			>56.5				
Benzo(a)anthracene	82.1						
bis(2-ethylhexyl) phthalate	>98.8	>93.4	49	Increase		>41.2	>50
Butyl benzyl phthalate						>80.0	
Carbon tetrachloride				>44.4			
Chloroform	65			>48.6	>58.6	>16.7	CBD
Chrysene	>83.6						
Di-n-butyl phthalate	>95.8						
Di-n-octyl phthalate	>98.0		28.6	23.1			
Dichlorobenzene				>50.0			
Diethyl phthalate	>83.3						
Dioctyl phthalate				50			
Ethyl benzene				>90.0		CBD	CBD
Methylene chloride	89.2			>60	>62.5	>77.8	98.4
Naphthalene				>71.4			
Phenanthrene	>41.2						
Phenol	>90.9			Increase		74	94
Pyrene	>71.4						
Tetrachloroethylene	92			>92.3		>77.3	
Toluene	>85.7		>61.5	>98.5		>50.0	>16.7
Trichloroethylene	>47.4			>93.8		>93.3	>94.7

CBD = Cannot be determined.
Increase = Eff. Conc. > Inf. Conc.

Inorganics removal data for selected Indiana wastewater treatment plants are reported in Table 81. The removal efficiencies are among the lowest recorded in this review. The highest removal efficiencies were noted for copper, chromium and lead, while the lowest removals were noted for cadmium, nickel and cyanide.

TABLE 81. REMOVAL OF INORGANIC CONTAMINANTS BY SELECTED INDIANA WASTEWATER TREATMENT PLANTS (BRUMFIELD, 1986)

INORGANIC	REMOVAL (%)				
	COLUMBUS	CRAWFORDS-VILLE	ELKHART	MICHIGAN CITY	SPEEDWAY
Cadmium	50	0	7.7	6.7	75
Chromium	88	25	34	34	66
Copper	79	32	44	29	48
Mercury	65	-	23	-	0
Nickel	36	27	16	Increase	Increase
Lead	55	31	26	0	84
Zinc	52	65	6	38	Increase
Cyanide	Increase	Increase	15	99	30

Increase = Eff. conc. > Inf. conc.

Metal removals at two Milwaukee, WI treatment plants are listed in Table 82. Removal efficiencies for chromium were nearly identical at the two plants and the same was true for copper. Cadmium removal was much higher at the Jones Island plant than at the South Shore plant, due to higher influent levels at the former plant.

TABLE 82. ANNUAL REMOVAL OF SELECTED HEAVY METALS BY MILWAUKEE WASTEWATER TREATMENT PLANTS (KLEINERT, 1986)

METAL	YEAR	JONES ISLAND (% Removal)	SOUTH SHORE (% Removal)
Cadmium	1975	67	35
	1976	73	67
	1977	84	65
	1978	78	42
	1979	84	Increase
	1980	87	36
	1981	77	40
	1982	73	44
	1983	74	29
	Grand Mean	77 ± 6.5	39 ± 22
Chromium	1975	81	73
	1976	85	84
	1977	90	87
	1978	90	72
	1979	92	92
	1980	95	91
	1981	94	94
	1982	93	95
	1983	93	93
	Grand Mean	90 ± 4.6	87 ± 8.7
Copper	1975	45	46
	1976	47	61
	1977	82	82
	1978	68	84
	1979	78	64
	1980	85	77
	1981	84	88
	1982	82	90
	1983	73	87
	Grand Mean	71 ± 16	75 ± 15

At the Madison WI wastewater treatment plant, metal removal efficiencies for the period 1979 to 1982 have been summarized and appear in Table 83. Cadmium, copper, lead and zinc concentrations were reduced by 70 percent or more, on average. Mean removal efficiencies for chromium and nickel were considerably lower at 38 and 37 percent, respectively.

TABLE 83. ANNUAL METAL REMOVALS BY MADISON, WISCONSIN WASTEWATER TREATMENT PLANT (KLEINERT, 1986)

METAL	YEAR	% REMOVAL
Cadmium	1979	73
	1980	79
	1981	75
	1982	95
	Grand Mean	81
Chromium	1979	0
	1980	25
	1981	60
	1982	68
	Grand Mean	38
Copper	1979	86
	1980	83
	1981	83
	1982	84
	Grand Mean	84
Mercury	1979	71
	1980	69
	1981	47
	1982	67
	Grand Mean	63
Nickel	1979	48
	1980	51
	1981	24
	1982	27
	Grand Mean	37
Lead	1979	80
	1980	80
	1981	74
	1982	74
	Grand Mean	77
Zinc	1979	75
	1980	68
	1981	63
	1982	77
	Grand Mean	71

Removal efficiencies for trace organic contaminants in selected Wisconsin wastewater treatment plants are presented in Table 84. The removal efficiencies were generally high (e.g. greater than 70 percent) and in this data set, no organic compound had a consistently low removal efficiency. Compounds such as trichloroethylene, ethyl benzene and butylbenzyl phthalate were removed efficiently on a regular basis.

TABLE 84. REMOVAL OF ORGANIC CONTAMINANTS BY SELECTED WISCONSIN WASTEWATER TREATMENT PLANTS (KLEINERT, 1986)

COMPOUND	REMOVAL (%)					
	JONES ISLAND	SOUTH SHORE	RACINE	MADISON	KENOSHA	GREEN BAY
Methylene chloride	Increase	Increase	-	74	25	-
1,2-t-Dichloroethylene	>86	-	>96	-	-	-
Chloroform	9	Increase	50	>95	-	Increase
1,1,1-Trichloroethane	>81	36	71	-	86	>94
Trichloroethylene	82	89	>97	-	-	>96
Benzene	Increase	44	>92	-	-	-
Toluene	31	89	>93	>92	>50	>99.5
Ethyl benzene	>73	>97	>91	-	>75	>96
Tetrachloroethylene	-	Increase	88	-	>75	>96
1,3-Dichloropropylene	-	>95	-	-	-	-
Carbon tetrachloride	-	-	>82	-	-	-
Chlorobenzene	-	-	>86	-	-	-
Chlorodibromomethane	-	-	>73	-	-	-
1,1-Dichloroethane	-	-	>93	-	-	-
1,1-Dichloroethylene	-	-	>93	-	-	-
1,2-Dichloropropane	-	-	>86	-	-	-
Trichlorofluoromethane	-	-	>95	-	-	-
Phenol	>99.7	-	-	-	-	-
Pentachlorophenol	>82	-	-	-	-	-
1,3-Dichlorobenzene	-	>84	-	-	-	-
1,4-Dichlorobenzene	95	>67	57	-	-	-
1,2-Dichlorobenzene	>80	>38	-	-	-	-
Diethyl phthalate	65	72	Increase	-	-	>98
Dimethyl phthalate	-	>67	-	-	-	-
Di-n-butyl phthalate	87	87	Increase	-	-	>90
Butyl benzyl phthalate	>87	>93	-	-	-	>99.3
Bis(2-ethyl hexyl) phthalate	77	75	Increase	35	92	>97
Naphthalene	>97	>82	-	-	-	-
Fluoranthene	>86	>67	-	-	-	-
Phenanthrene/Anthracene	-	63	-	-	-	-
Fluorene	>86	>76	-	-	-	-
Pyrene	-	>67	-	-	-	-
Chrysene	>88	-	-	-	-	-
Benzo(a)anthracene	-	>64	-	-	-	-
alpha-BHC	-	-	>80	-	-	-
Dieldrin	-	-	>92	-	-	-
Heptachlor epoxide	-	-	Increase	-	-	-
delta-BHC	-	-	-	-	67	-
Endosulfan I	-	-	-	-	>85	-
4,4'-DDT	-	-	-	-	96	-
Aldrin	-	-	-	-	-	>10
Hexachlorobenzene	-	-	-	-	-	>90

Increase = Eff. conc. > Inf. conc.

The removal of various contaminants in a number of full-scale or pilot-scale studies are summarized in Table 85. For comparison the estimated overall removals of contaminants by activated sludge plants with both acclimated and unacclimated biomass from the EPA (1986) Report to Congress are also presented in Table 85. Removal efficiences estimated by the EPA (1986) were based on physical/chemical properties of the organic compounds, observed concentrations in sludges from the 40 POTW study (EPA, 1982a), and potential biodegradability. Purgeable compounds were typically removed to a high degree (greater than 80 percent), although some compounds such as chlorobenzene, 1,1,2-trichloroethane, chloroform and methylene chloride had lower removal efficiencies in some studies (EPA, 1982a, 1982b; Petrasek _et al_, 1983a; Hannah _et al_, 1986). Again, this may result from analyzing chlorinated effluents in some cases.

TABLE 85. REMOVAL OF TRACE CONTAMINANTS BY BIOLOGICAL WASTEWATER TREATMENT PLANTS

SUBSTANCE	CONTAMINANT REMOVAL (%)											
	40 PLANT STUDY (EPA, 1982a)	EPA 30 DAY STUDY (EPA, 1982b)	EPA REPORT TO CONGRESS (EPA, 1986)		HAMILTON, ONTARIO (CANVIRO, 1984)	PETRASEK ET AL. (1983b)	PETRASEK ET AL. (1983a)	HANNAH ET AL. (1986)	PETRASEK & KUGELMAN (1983)	ROMAN-SEDA (1984)	AUSTIN ET AL. (1985)	NEILSEN & HRUDEY (1983)
			ACCLIMATED	UNACCLIMATED								
Acrylonitrile												
Benzene	74.7	78	95	90			>99					
Toluene	86.3	83	95	90			>99					
Ethyl benzene	82.4	81	95	90			>99	93				
Carbon tetrachloride		CBD	90	85			>99	74				
Chlorobenzene		60	90	90			>99					
1,2-Dichloroethane		CBD	90	50				84				
1,1,1-Trichloroethane	81.9	75	95	90			>99					
1,1-Dichloroethane		CBD	90	80				94				
1,1-Dichloroethylene		96	95	90			>99	92				
1,1,2-Trichloroethane		36	80	25			80					
1,1,2,2-Tetrachloroethane		78	90	25			94					
Chloroethane		CBD										
Chloroform	65.2	49	90	80			>97	86				
1,2-Dichloropropane		CBD	90	70			>98					
1,3-Dichloropropane		CBD										
Methylene chloride	57.1	8					>97					
Methyl chloride		>92										
Methyl bromide												
Bromoform								65				
Dichlorobromomethane							>99					
Trichlorofluoromethane		CBD	95	90								
Dichlorodifluoromethane			95	95								
Chlorodibromomethane		CBD					>88					
Tetrachloroethylene	72.2	86	90	85			94					
Trichloroethylene	84.8	84	95	87			<99					
Vinyl chloride		>96	95	95								
1,2-t-Dichloroethylene	68.7	CBD	90	80								
1,2-Dichlorobenzene		CBD	90	87								
1,3-Dichlorobenzene		36	90	87								
1,4-Dichlorobenzene		84	90	87								
Hexachloroethane		CBD										
Hexachlorobenzene		CBD										

TABLE 85. REMOVAL OF TRACE CONTAMINANTS BY BIOLOGICAL WASTEWATER TREATMENT PLANTS (cont'd)

SUBSTANCE	CONTAMINANT REMOVAL (%)											
	40 PLANT STUDY (EPA, 1982a)	EPA 30 DAY STUDY (EPA, 1982b)	EPA REPORT TO CONGRESS (EPA, 1986)		HAMILTON, ONTARIO (CANVIRO, 1984)	PETRASEK ET AL, (1983b)	PETRASEK ET AL, (1983a)	HANNAH ET AL, (1986)	PETRASEK & KUGEL-MAN (1983)	ROMAN-SEDA (1984)	AUSTIN ET AL, (1985)	NEILSEN & HRUDEY (1983)
			ACCLIMATED	UNACCLIMATED								
1,2,4-Trichlorobenzene		62	85	85								
Bis(2-chloroethxy) methane		96										
Naphthalene	68.9	94	95	75	95	99		97				
2-Chloronaphthalene		CBD										
Isophorone		CBD						98				
Nitrobenzene												
2,6-Dinitrotoluene		CBD										
Bis(2-ethylhexyl) phthalate	67.4	20	90	90		79		87				
Di-n-octyl phthalate		Increase	90	90		83						
Dimethyl phthalate		Increase	95	65		98						
Diethyl phthalate	62.2	Increase	90	75		97						
Di-n-butyl phthalate	61.9	68	90	90		94		88				
Acenaphthylene		84			99.9							
Acenaphthene		92				97						
Butylbenzyl phthalate	67.9	CBD	95	90		96						
Fluorene		88			98	98						
Fluoranthene		84			96	94		95				
Chrysene		CBD				97						
Pyrene	86.6	CBD			95	94		95				
Phenanthrene	65.9	CBD				97		95				
Anthracene	69.5	CBD	95	90		97						
Benzo(a)anthracene		>50				98						
Benzo(b)fluoranthene												
Benzo(k)fluoranthene		CBD										
Benzo(a)pyrene		CBD			99							
Indeno(1,2,3-c,d)pyrene		CBD										
Dibenzo(a,h)anthracene												
4-Chlorophenyl phenyl ether		CBD										
Bis(2-chloroethyl) ether		CBD						80				
Bis(2-chloroisopropyl) ether		CBD										
Benzidine		CBD										
Carbazole					98							

CBD = Cannot be determined. Increase = Negative removal.

TABLE 85. REMOVAL OF TRACE CONTAMINANTS BY BIOLOGICAL WASTEWATER TREATMENT PLANTS (cont'd)

SUBSTANCE	CONTAMINANT REMOVAL (%)											
	40 PLANT STUDY (EPA, 1982a)	EPA 30 DAY STUDY (EPA, 1982b)	EPA REPORT TO CONGRESS (EPA, 1986)		HAMILTON, ONTARIO (CANVIRO, 1984)	PETRASEK ET AL, (1983b)	PETRASEK ET AL, (1983a)	HANNAH ET AL, (1986)	PETRASEK & KUGEL-MAN (1983)	ROMAN-SEDA (1984)	AUSTIN ET AL, (1985)	NEILSEN & HRUDEY (1983)
			ACCLIMATED	UNACCLIMATED								
1,2,4-Trichlorobenzene		62	85	85								
Bis(2-chloroethxy) methane		96										
Naphthalene	68.9	94	95	75	95	99		97				
2-Chloronaphthalene		CBD										
Isophorone		CBD						98				
Nitrobenzene												
2,6-Dinitrotoluene		CBD										
Bis(2-ethylhexyl) phthalate	67.4	20	90	90		79		87				
Di-n-octyl phthalate		increase	90	90		83						
Dimethyl phthalate		increase	95	65		98						
Diethyl phthalate	62.2	increase	90	75		97						
Di-n-butyl phthalate	61.9	68	90	90		94		88				
Acenaphthylene		84			99.9							
Acenaphthene		92				97						
Butylbenzyl phthalate	67.9	CBD	95	90		96						
Fluorene		88			98	98						
Fluoranthene		84			96	94		95				
Chrysene		CBD				97						
Pyrene	86.6	CBD			95	94		95				
Phenanthrene	65.9	CBD				97		95				
Anthracene	69.5	CBD	95	90		97						
Benzo(a)anthracene		>50				98						
Benzo(b)fluoranthene												
Benzo(k)fluoranthene		CBD										
Benzo(a)pyrene		CBD			99							
Indeno(1,2,3-c,d)pyrene		CBD										
Dibenzo(a,h)anthracene												
4-Chlorophenyl phenyl ether		CBD										
Bis(2-chloroethyl) ether		CBD						80				
Bis(2-chloroisopropyl) ether		CBD										
Benzidine		CBD										
Carbazole					98							

CBD = Cannot be determined. Increase = Negative removal.

Removal data reported for base-neutral extractable compounds has chiefly centered on PAHs and phthalate esters. The degree of removal reported varies from one study to another. Removals typically greater than 80 percent were reported by Petrasek et al (1983b) and Hannah et al (1986). Removal efficiencies were not as high in either the 40 POTW study (EPA, 1982a) or the 30 day study (EPA, 1982b). Naphthalene was the only PAH in which the removal was consistently high. In studies by Petrasek et al (1983b), Hannah et al (1986), CANVIRO Consultants Ltd. (1984) and in the 30 day study at Nashville (EPA, 1982b), the removal efficiency of PAHs was generally at least 80 percent and frequently 90 percent or higher.

Removal efficiencies for the acid extractable compounds are not well characterized in Table 85 except for phenol and pentachlorophenol. The removal of phenol was consistently high in the studies reviewed. The removal of pentachlorophenol was quite variable, ranging from 19 percent in the study by Petrasek et al (1983b) to 96 percent (Hannah et al, 1986). According to the removal estimates provided by the EPA (1986), the variable removal may depend on the stage of acclimation of the mixed liquor to pentachlorophenol. In the 30 day study (EPA, 1982b), removal efficiences ranged from negative removal (4-nitrophenol; 2,4-dimethylphenol) to 93 percent (2-chlorophenol; pentachlorophenol).

Little data on removals of the pesticide/PCB group have been reported. Removal efficiencies for Lindane ranged from 18 percent (Hannah et al, 1986) to 70 percent in the study at Hamilton, Ontario (CANVIRO Consultants, 1984a). Petrasek et al (1983b) reported removals for heptachlor, toxaphene and the PCB mixture Aroclor 1254 in the range of 93 to 98 percent.

With respect to metals, copper and chromium were observed with consistently high removals of greater than 70 percent in Table 85. Arsenic removals were variable ranging from 19 percent (Petrasek and Kugelman, 1983) to 85 percent (CANVIRO, 1984a); cadmium similarly had variable removal efficiencies reported in the literature, from 24 to 92 percent. Lead, mercury and zinc were also removed by the activated sludge process over a broad range of 50 to 95 percent. Nickel was removed to a modest extent, but consistently in the range of 43 to 62 percent. Cyanide removal was observed over a range of 0 percent in the 30 day study (EPA, 1982b) to 65 percent for the 40 POTW study (EPA, 1982a).

The variabilities of removal efficiencies between activated sludge plants in the EPA 40 POTW study (EPA, 1982a) are summarized in Table 86 (Unger and Claff, 1985). Relative standard deviation values ranged from 21 to 50 percent. One interesting observation with the metals data was that nickel, which had the lowest mean removal efficiency, also exhibited the most variable removal, whereas chromium, copper and zinc, which were the metals removed to the greatest extent, had the least variable removal efficiencies. This phenomenon is probably related to pH and solubility of the metals. A similar relationship was observed between removal rates and the variability of removal efficiencies (i.e. inversely proportional) for organic compounds. The RSDs of the mean percent removals range from 10 to 42 percent. Analyses of the data indicated that with the exception of bis(2-ethylhexyl) phthalate, the removal efficiencies of individual pollutants were statistically different at the 0.05 percent confidence level between activated sludge plants. Unger and Claff (1985) concluded that for an accurate

TABLE 86. MEAN CONTAMINANT REMOVAL RATES AND REMOVAL VARIABILITY IN ACTIVATED SLUDGE PLANTS (UNGER AND CLAFF, 1985)

CONTAMINANT	MEAN REMOVAL (%)	RSD (% of Mean)
Metals		
Arsenic	43.7	38.7
Cadmium	65.9	34.9
Chromium	77.5	21.3
Copper	80.8	22.9
Lead	57.0	35.9
Mercury	60.2	33.1
Nickel	42.7	50.4
Selenium	49.7	39.1
Silver	67.7	32.0
Zinc	75.3	21.4
Cyanide	64.3	35.1
Volatiles		
Benzene	74.7	28.2
1,1,1-Trichloroethane	81.9	17.3
Chloroform	65.2	30.7
1,2-trans-Dichloroethylene	68.7	31.4
Volatiles (cont'd)		
Ethylbenzene	82.4	20.0
Methylene Chloride	57.1	41.7
Tetrachloroethylene	72.2	33.4
Toluene	86.3	19.0
Trichloroethylene	84.8	19.0
Acid-Extractable		
Phenol	83.9	22.7
Base-Neutrals		
Naphthalene	68.9	33.3
Bis(2-ethylhexyl)phthalate	67.4	32.3
Butylbenzyl Phthalate	67.9	33.1
Di-n-butyl Phthalate	61.9	38.7
Diethyl Phthalate	62.2	41.5
Anthracene	69.5	31.4
Phenanthrene	65.9	33.5
Pyrene	86.6	10.0

assessment of removal efficiency, data should be determined for each individual treatment plant rather than relying on mean removal estimates considered representative of all plants.

This conclusion has implications for computerized programs which assume a relatively consistent removal efficiency between treatment plants for any particular contaminant. Specifically a program such as the Sewer Use Bylaw Assistance System (Simcoe Engineering Ltd., 1984), which at present assumes a "typical" removal for contaminants at wastewater treatment plants, may need to be revised to permit the entry of contaminant removal efficiencies at each treatment plant. The program would then be more capable of addressing the maximum concentration of a contaminant permitted to enter a treatment plant.

Removal efficiencies for metals in seven California treatment plants are summarized in Table 87 (Austin et al, 1985). Mean removals and the variability (RSD values) of the removals are also recorded. Cyanide, nickel and cadmium had the lowest mean removal efficiencies while copper and zinc were removed at the highest rates. In agreement with the observations of Unger and Claff (1985), the results of the California study indicated that the least amount of variability was associated with the highest mean removal efficiencies, and contaminants with the lowest mean removals were the most variable (Austin et al, 1985).

Higher removal efficiencies in these cases usually result from raw wastewater concentrations that are substantially higher than effluent concentrations. For example, if an influent concentration is ten times greater than the effluent concentration (say 100 ug/L and 10 ug/L, respectively), the difference in removal efficiencies will not be large if the influent varies by 10 ug/L. If the influent concentration is only twice as great as the effluent concentration (e.g. 20 ug/L and 10 ug/L, respectively), however, a variation of 10 ug/L in the influent concentration will result in substantial variation in the removal. These situations can occur when influent and effluent concentrations approach the detection limit.

A second approach using linear regression for estimation of contaminant removal variability was examined in two studies funded by the U.S. Environmental Protection Agency. In the 30 day study at the Chattanooga Moccasin Bend treatment plant (EPA, 1982b), daily composite samples were collected. Concentrations in the raw wastewater and final effluent samples were correlated without a time lag period. The same procedure was applied in correlating influent and effluent trace contaminant concentrations during the 40 POTW study (EPA, 1982a). The correlation coefficients resulting from these linear regressions are summarized in Table 88.

In the 30 d study, strong correlations between influent and effluent contaminant concentrations were noted for cadmium, chromium, toluene, 1,1,1-trichloroethane and diethyl phthalate (EPA, 1982a). Strong correlations between influent and effluent concentrations emerged from the 40 plant study for cadmium, nickel, zinc, 1,1,1-trichloroethane, tetrachloroethylene, chloroform, methylene chloride and trichloroethylene (EPA, 1982a). Only cadmium and 1,1,1-trichloroethane exhibited strong correlations in both studies, whereas the correlations for contaminants such as zinc, toluene, methylene chloride and trichloroethylene were strong in one study, but not in the other.

TABLE 87. REMOVAL OF INORGANIC CONTAMINANTS BY CALIFORNIA WASTEWATER TREATMENT PLANTS (AUSTIN ET AL, 1985)

INORGANIC	REMOVAL BY TREATMENT PLANT (%)							MEAN (% Removal)	S.D. (% Removal)	R.S.D. (% of Mean)
	POMONA	SAN JOSE CREEK	WHITTIER NARROWS	LOS COYOTES	LONG BEACH	SAUGUS	VALENCIA			
Arsenic	57	48	77	60	42	-	-	57	13	24
Cadmium	30	43	78	83	19	21	17	42	28	67
Chromium	80	81	93	93	43	69	68	75	17	23
Copper	93	94	95	91	85	90	87	91	4	4
Lead	78	78	81	76	52	39	30	62	21	34
Nickel	40	55	57	63	21	33	22	42	17	41
Silver	83	74	81	86	81	60	72	77	9	12
Zinc	74	83	84	92	76	82	73	81	7	9
Cyanide	20	23	64	0	0	-	-	21	26	120

TABLE 88. LINEAR CORRELATION OF INFLUENT AND EFFLUENT TRACE CONTAMINANT CONCENTRATIONS (EPA, 1982a; 1982b)

CONTAMINANT	CORRELATION COEFFICIENT (r)	
	30 d STUDY CHATTANOOGA (EPA, 1982b)	40 POTW STUDY (EPA, 1982a)
Metals		
Cadmium	0.943	0.966
Chromium	0.913	0.402
Silver	0.596	0.523
Lead	0.524	0.354
Nickel	0.396	0.795
Cyanide	0.080	0.102
Zinc	0.163	0.855
Copper	0.041	0.536
Mercury	-0.008	0.329
Volatiles		
1,1,1-Trichloroethane	0.804	0.996
Toluene	0.730*	0.059
Benzene	0.597	0.082
Tetrachloroethylene	0.535	0.966
Chloroform	0.484	0.837
Ethylbenzene	0.340*	0.558
1,2-Trans-Dichloroethylene	0.322	0.442
Methylene Chloride	0.22	0.977
Trichloroethylene	0.081	0.899
Acids		
2,4-Dichlorophenol	0.624	-
Phenol	0.480*	0.287
Base/Neutrals		
Diethyl Phthalate	0.779	0.476
1,4-Dichlorobenzene	0.654	-
Naphthalene	0.634	0.589
Phenanthrene	0.472	-
1,2,4-Trichlorobenzene	0.383	-
Di-N-Butyl Phthalate	0.228	0.243
1,3-Dichlorobenzene	0.114	-
Bis(2-Ethylhexyl) Phthalate	0.020*	0.669
Butyl benzyl Phthalate	-	0.207

* Outlier values are not included in correlation.

The results of these regression analyses indicate that in a very few cases, effluent concentrations can be predicted from influent levels. For most contaminants however, the correlation was poor. In other words, the removal efficiency was not constant, but highly variable for most contaminants. This implies that the effluent concentrations were not a function of the influent levels, but fluctuated independently of the influent concentrations.

In other studies (Table 89), 71 percent (mass basis) of a shock load of hexavalent chromium passed through a full-scale activated sludge plant (Henney et al, 1980). In bench-scale activated sludge studies, cadmium removals ranged from 65 to 88 percent when the sludge age varied from 3 to 18 days (Lawson et al, 1984). Both nickel and copper were poorly removed,

TABLE 89. SUMMARY OF ADDITIONAL CONTAMINANT REMOVAL STUDIES

CONTAMINANT	REMOVAL EFFICIENCY (%)	SCALE	COMMENTS	REFERENCE
Chromium	29	Full	-Shock load from electroplater removal on mass basis	Henney et al (1980)
Cadmium	65 to 88	Bench	-Sludge age varied from 3 to 18 days	Lawson et al (1984)
Nickel	0 to 26			
Copper	0 to 42			
Copper	65 to 88	Bench		Hunter et al (1983)
Cadmium	8 to 80	Pilot	-Spiked & unspiked samples; sludge age 4 to 12 days	Rossin et al (1982)
Chromium	10 to 68			
Copper	70 to 84			
Nickel	11 to 36			
Lead	32 to 82			
Zinc	39 to 68			
Chloroform	93	Pilot		Argaman & Koon (1983)
Chlorophenoxy Herbicides	<20	Pilot		Hill et al (1986)
2,4-D	16 to 55	Pilot		Saleh et al (1980)
Hexachlorobicycloheptene	87	Full	-Industrial contaminants	Lurker et al (1982)
Heptachlorobicycloheptene	91			
Chlordene	92			
Azo dye	90	Pilot		Shaul et al (1985)
Octadecyltrimethylammonium chloride	96 to 98	Bench	-Surfactant compound	Games et al (1982)

with the extent of removal ranging from 0 to 26 percent for nickel and 0 to 42 percent for copper. The reduction of copper observed by Lawson et al, (1984) was low compared with the results observed in the other studies summarized in Table 85. The removal of copper in another set of bench-scale activated sludge tests ranged from 65 to 88 percent (Hunter et al, 1983). In both control and spiked wastewater in pilot-scale studies, copper and lead removal were greater than 65 percent (Rossin et al, 1982). Nickel was poorly removed at 11-36 percent. Removals of cadmium, chromium and zinc were intermediate.

The observed removal rate of chloroform in a pilot-scale diffused air activated sludge plant was 93 percent compared with the removal in a full-scale treatment plant which averaged 94 percent chloroform removal (Argaman and Koon, 1983). A surfactant compound, octadecyltrimethylammonium chloride was removed to the extent of 96 to 98 percent in bench-scale activated sludge tests (Games et al, 1982).

The removal efficiencies of the chlorinated hydrocarbon compounds hexachlorobicycloheptene (Hex-BHC), heptachlorbicycloheptene (HCBCH) and chlordene by a full-scale contact stabilization plant were 87 percent for hex-BHC, 91 percent for HCBCH, and 92 percent for chlordene (Lurker et al, 1982). In a pilot-scale activated sludge plant the removal of chlorophenoxy herbicides was typically less than 20 percent (Hill et al, 1986). Removal of 2,4-D by a pilot-scale activated sludge plant ranged from 16 percent to 55 percent (Saleh et al, 1980). Azo dyes were reduced by 89 to 90 percent in a small pilot-scale activated sludge system (Shaul et al, 1985).

4.2 Observed Removals by Other Wastewater Treatment Processes

4.2.1 Primary Treatment

Concentrations and removal efficiencies of purgeable organics at a pilot plant facility are reported in Table 90 (Petrasek et al, 1983a). The primary effluent levels in unspiked trial runs were usually less than 35 ug/L, and removals ranged from 14 percent removal (chlorobenzene) to 88 percent removal (tetrachloroethylene and tetrachloroethane). In the spiked wastewater experiments, primary effluent concentrations up to 295 ug/L of 1,2-dichloropropane were recorded. Removal efficiencies in the primary clarifiers were considerably lower than in secondary treatment, ranging from 0 percent (chloroform, 1,1,2-trichloroethane, and tetrachloroethylene/tetrachloroethane) to 57 percent for 1,1-dichloroethylene.

In a pilot-scale activated sludge plant, semi-volatile extractable organics, spiked into the wastewater, were poorly removed if at all, by primary clarification (Petrasek et al, (1983b). Influent and primary effluent concentrations are summarized in Table 91.

In comparing the performance of several wastewater treatment processes, Hannah et al (1986) examined the removal of trace contaminants by primary clarification. Raw wastewater was spiked with a cocktail of the contaminants before testing. The results of the program are summarized in Table 92. Contaminant removals by primary clarification ranged from 0 for 1,1-dichloroethane, chloroform and lindane, to 45 percent for phenol.

TABLE 90. REMOVAL OF PURGEABLE CONTAMINANTS BY PRIMARY CLARIFICATION (PETRASEK ET AL, 1983a)

COMPOUND	CONTROL RUNS			SPIKED RUN		
	INFLUENT (ug/L)	PRIMARY EFFLUENT (ug/L)	REMOVAL BY PRIMARY CLARIFIER (percent)	INFLUENT (ug/L)	PRIMARY EFFLUENT (ug/L)	REMOVAL BY PRIMARY CLARIFIER (percent)
Methylene Chloride	<30.6	<22.3	27	118	89	25
1,1-Dichloroethene	<10.7	<3.7	65	79	34	57
Chloroform	10.8	7.2	33	137	143	0
Carbon Tetrachloride	<6.2	<3.3	47	60	32	47
1,2-Dichloropropane	<0.2	<0.3	-	309	295	5
Trichloroethylene	<4.2	<2.9	31	107	68	36
1,1,2-Trichloroethane	<2.9	<0.5	83	133	155	0
Dibromochloromethane	<0.6	<0.3	50	58	49	16
Benzene	<2.7	<2.7	-	73	61	16
1,1,1-Trichloroethane	<65.0	34.2	48	132	96	27
Bromodichloromethane	<0.2	<0.2	-	89	64	28
Chlorobenzene	102	87.3	14	197	163	17
Tetrachloroethylene & Tetrachloroethane	<24.0	<2.8	88	252	263	0
Toluene	160	114	29	255	198	22
Ethylbenzene	<24.5	7.3	70	82	69	16

TABLE 91. REMOVAL OF SEMI-VOLATILE EXTRACTABLE COMPOUNDS BY PRIMARY CLARIFICATION (PETRASEK ET AL, 1983b)

COMPOUND	CONCENTRATION (ug/L)	
	INFLUENT	PRIMARY EFFLUENT
Pesticides/PCBs		
Aroclor 1254	<33.5	<114.0
Heptachlor	31.7	<28.5
Lindane	45.5	<41.8
Toxaphene	<47.4	<87.5
Phenols		
2,4-Dimethylphenol	95.7	60.9
Phenol	261.3	>196.2
Pentachlorophenol	7.6	13.0
Phthalates		
Bis(2-ethylhexyl) phthalate	51.7	52.4
Butylbenzyl phthalate	33.5	37.5
Diethyl phthalate	46.4	57.7
Dimethyl phthalate	47.3	<37.2
Di-n-butyl phthalate	43.8	54.4
Di-n-octyl phthalate	28.2	<34.4
Polynuclear Aromatic Hydrocarbons		
Acenaphthylene	39.8	53.6
Anthracene	34.8	33.9
Benzo(a)anthracene	23.8	24.9
Chrysene	38.9	36.6
Fluoranthene	30.6	39.9
Fluorene	37.9	51.6
Naphthalene	76.7	99.7
Phenanthrene	40.4	44.3
Pyrene	30.4	39.1

TABLE 92. REMOVAL OF TRACE CONTAMINANTS BY PRIMARY CLARIFICATION (HANNAH ET AL, 1986)

COMPOUND	WASTEWATER FEED		PRIMARY EFFLUENT		PRIMARY CLARIFICATION	
	$\bar{X}$ (ug/L)	σ	$\bar{X}$ (ug/L)	σ	% REMOVAL	σ
Carbon tetrachloride	69	33	63	40	19	34
1,1-Dichloroethane	144	24	144	16	-2	17
1,1-dichloroethylene	212	72	188	69	5	31
Chloroform	135	16	143	17	-7	15
1,2-Dichloroethane	153	44	135	41	7	14
Bromoform	90	35	83	37	18	23
Ethyl benzene	111	21	102	25	9	18
Bis(2-ethylhexyl) phthalate	168	74	90	32	37	33
Dibutyl phthalate	73	26	68	19	2	20
Naphthalene	108	34	92	33	13	23
Phenanthrene	95	24	76	35	21	21
Pyrene	104	18	84	22	18	21
Fluoranthene	104	19	80	21	22	20
Isophorone	89	30	77	19	4	17
Bis(2-chloroethyl)ether	143	51	122	37	6	27
p-Dichlorobenzene	93	17	75	24	19	18
Phenol	126	49	112	70	23	48
2,4-Dichlorophenol	228	178	133	105	45	24
Pentachlorophenol	84	46	78	50	16	28
Lindane	39	6	40	11	-4	25
Heptachlor	39	3	26	1	32	7
Chromium	221	88	206	135	7	
Copper	345	119	278	113	19	
Nickel	141	93	136	101	4	
Lead	165	168	115	102	30	
Cadmium	25	23	22	14	12	

$\bar{X}$ = Mean Concentration

σ = Standard Deviation of mean.

Because the wastewater was spiked, evaluation of contaminant concentration variability is not meaningful. The variability of the mean removal data is of interest however. The standard deviations are frequently greater than mean removal values, indicating that the removal efficiency is highly variable. The most consistent removal was found with heptachlor. The most widely varying removal was associated with di-n-butyl phthalate, in which the standard deviation was an order of magnitude greater than the mean.

During primary clarification studies, 6 chlorinated phenoxy herbicides were spiked into wastewater to provide a 10 ug/L concentration (Hill et al, 1985). Removal of the herbicides was usually less than 25 percent. In almost all test runs, the removal of 2,4-D was less than 20 percent. The range of concentrations of PCBs and organochlorine insecticides investigated in raw wastewater and primary effluent samples from the United Kingdom, and typical removal efficiencies are reported in Table 93 (McIntyre et al, (1981). The pesticide/PCB levels observed were in the ng/L range. Typical removal efficiencies were 50, 48 and 30 percent for PCBs, dieldrin and p,p'-DDE, respectively. It was concluded that the removal of the organochlorine compounds were similar in magnitude to removals of suspended solids, but no statement was made regarding the removal mechanism.

TABLE 93. CONCENTRATION RANGES AND TYPICAL REMOVALS OF ORGANO-PESTICIDES AND PCBs DURING PRIMARY CLARIFICATION (McINTYRE ET AL, 1981)

WASTE STREAM	PCBs	p,p'-DDE	DIELDRIN
Raw Wastewater (ug/L)	0.047 - 0.082	0.020 - 0.031	0.024 - 0.039
Primary Effluent (ug/L)	0.018 - 0.036	0.011 - 0.026	0.012 - 0.022
Removal Efficiency (%)	50.4	29.6	48.2

In primary clarifiers, the two mechanisms for contaminant removal are sedimentation and volatilization. Because the vapour pressures of the pesticides and PCBs are very low, volatilization is not expected to be a significant removal mechanism. Because the removal efficiencies of the suspended solids and pesticides/PCBs were observed to be similar in the United Kingdom (McIntyre et al, 1981), it appears that sedimentation is the principal removal mechanism for these compounds.

The removal of phenol by primary clarification in an activated sludge plant in Puerto Rico was 33 percent at an average influent level of 865 ug/L (Roman-Seda, 1984).

4.2.2 Trace Contaminant Removal by Other Treatment Processes

The removals of contaminants by other wastewater processes are summarized in Table 94 (Hannah et al, 1986). The facultative lagoon performed well in the removal of the trace contaminants in all classes of contaminants. The aerated lagoon removed most classes of contaminants with the exception of phenolic compounds. The trickling filter was less successful in

TABLE 94. REMOVAL OF TRACE CONTAMINANTS BY DIFFERENT WASTEWATER TREATMENT PROCESSES (HANNAH ET AL, 1986)

COMPOUND	PRIMARY PLUS FILTRATION		CHEMICAL CLARIFICATION		TRICKLING FILTER		AERATED LAGOON		FACULTATIVE LAGOON	
	% REMOVAL	σ	% REMOVAL	σ	% REMOVAL	σ	% REMOVAL	σ	% REMOVAL	σ
Carbon Tetrachloride	22	37	-13	24	59	22	70	27	77	24
1,1-Dichloroethane	32	9	21	14	34	12	68	4	87	4
1,1-Dichloroethylene	22	21	25	30	58	16	60	22	85	17
Chloroform	18	9	20	15	25	18	61	11	80	7
1,2-Dichloroethane	34	9	22	31	33	16	70	14	90	7
Bromoform	2	27	-6	20	57	16	80	11	84	11
Ethylbenzene	35	28	31	34	71	9	70	21	96	5
Bis(2-ethylhexyl)phthalate	75	13	89	14	75	9	77	29	80	31
Dibutylphthalate	22	15	31	20	26	16	40	20	78	13
Naphthalene	20	19	23	16	28	16	64	12	87	8
Phenanthrene	49	14	74	7	45	15	55	19	82	19
Pyrene	61	8	88	4	54	8	63	14	75	12
Fluoranthene	61	8	87	4	53	11	64	15	77	11
Isophorone	8	21	5	25	17	36	22	37	25	32
Bis(2-chloroethyl)ether	20	28	17	40	-1	16	23	31	43	14
p-Dichlorobenzene	29	19	28	19	36	18	65	13	87	6
Phenol	4	33	21	56	50	29	30	42	86	11
2,4-Dichlorophenol	-4	6	60	15	31	33	48	46	73	38
Pentachlorophenol	19	36	90	38	4	6	37	36	74	12
Lindane	-	-	17	10	13	11	42	12	80	4
Heptachlor	-	-	64	3	53	4	66	5	62	6
Chromium	-	-	-	-	52	-	71	-	79	-
Copper	-	-	-	-	60	-	74	-	79	-
Nickel	-	-	-	-	30	-	35	-	43	-
Lead	-	-	-	-	48	-	58	-	50	-
Cadmium	-	-	-	-	28	-	-	-	32	-

σ = Standard Deviation

removing contaminants than either the facultative or aerated lagoon. Chemical clarification or primary treatment plus filtration did not remove much of the purgeable compounds. Chemical clarification removed successfully some base/neutral extractable compounds such as bis(2-ethylhexyl) phthalate, pyrene and fluoranthene, but not others. Primary filtration was not successful in removing either acid extractable compounds (phenols) or pesticides.

The concentrations removal of metals by oxidation ponds are reported in Table 95 (Suffern et al, 1981). Removal efficiencies for metals in the oxidation ponds ranged from 9 percent for cadmium to 88 percent for zinc. The highest removals were associated with the highest influent levels (zinc and copper). Effluent concentrations of zinc and copper were an order of magnitude higher than the other metal concentrations.

TABLE 95. TRACE METAL CONCENTRATIONS AND REMOVALS BY AN OXIDATION POND (SUFFERN ET AL, 1981)

METAL	INFLUENT (ug/L)	EFFLUENT (ug/L)	REMOVAL (%)
Cadmium	3.8	2.6	9
Chromium	2.8	1.2	57
Copper	110.	18.	84
Nickel	8.8	3.5	60
Lead	20.	5.6	72
Zinc	160.	20.	88

Higher concentrations of chloroform, carbon tetrachloride and trichloroethylene were recorded at the wet well and grit chambers of a full-scale treatment plant than above the aeration basins (Lurker et al, (1982). It was suggested that a substantial portion of these purgeables were released from the preliminary treatment stages.

In a rotating biological contactor, 64 percent of naphthalene was removed by the aerobic fixed film process based on recovery of ^{14}C-naphthalene (Glaze et al, (1985).

4.3 Mechanisms Contributing to Contaminant Removals

4.3.1 Metals

The removal of trace metal contaminants from wastewater in activated sludge plants is accomplished through two mechanisms, precipitation and adsorption. The relative importance of each removal mechanism is dependent on a number of factors including the trace metal, the concentration of the metal, the system pH, and the concentration and characteristics of the mixed liquor suspended solids.

Precipitation of metals in wastewater first occurs in the primary clarifiers. Some reported removals of trace metals by primary clarification are summarized in Table 96. The removals reported for each trace metal are highly variable and range from very little removal to 50 percent removal or higher. The reported removal efficiencies vary from one study to another. For example, removal efficiencies reported by Patterson and Kodukula (1984), Hannah et al (1986) and Petrasek

TABLE 96. REPORTED REMOVAL OF METAL CONTAMINANTS BY PRIMARY CLARIFICATION

CONTAMINANT	PATTERSON & KODUKULA (1984)	NEILSEN & HRUDEY(1) (1983)	HANNAH ET AL. (1986)	PETRASEK & KUGELMAN (1983)	ROMAN-SEDA (1984)	OLIVER & COSGROVE (1974)
Arsenic	N.D.	N.D.	N.D.	16	N.D.	N.D.
Cadmium	20	39	12	19	N.D.	60
Chromium	29	68	7	19	46	55
Copper	20	60	19	29	52	33
Mercury	N.D.	N.D.	N.D.	0	N.D.	60
Nickel	46	50	4	40	N.D.	15
Lead	42	N.D.	30	34	31	66
Zinc	18	44	N.D.	0	51	54

N.D. = No Data
(1) Geometric Mean

and Kugelman (1983) are typically lower for all contaminants than those reported by either Oliver and Cosgrove (1974) or Neilsen and Hrudey (1983).

The phase distribution of trace metals in wastewater has been considered as a factor influencing their removal in treatment plants. In general terms, lead, chromium and zinc are more insoluble, whereas cadmium, nickel and copper are more soluble (Rossin et al, 1982). The insoluble metals tend to be removed to a greater extent by primary clarification, and are less susceptible to adsorption by mixed liquor biomass than the soluble metals (Sterritt et al, 1981).

The concentration of the trace metal in aeration basins will influence the controlling removal mechanism (Brown and Lester, 1982a). In a study with four trace metals (cadmium, nickel, cobalt and manganese), they noted that at metal concentrations of 1,000 mg/L or less, precipitation was a significant removal mechanism relative to biosorption only for cadmium. When the metal concentration was increased to 10,000 mg/L, precipitation was a significant removal mechanism for all but nickel. These observations agree with the earlier findings of Cheng et al (1975), who suggested that at low metal concentrations, removal of the contaminants is accomplished by metal-organic complexes within the sludge flocs. At higher concentrations, precipitation became an important mechanism.

When the biomass concentration in the aeration tanks is low, however, precipitation may assume a more important role. Kodukula and Patterson (1984) reported that at low mixed liquor suspended solids levels, soluble metal concentrations are held at a relatively constant level by precipitation. As the solids concentration increases, higher soluble metal levels can exist, and biomass/metal interactions become more important for removal.

The ability of mixed liquor suspended solids to adsorb metals has been investigated using empirical models such as the Freundlich or Langmuir models (Cheng et al, 1975; Nelson et al, 1981; Brown and Lester, 1982a,b; Neilsen et al, 1984). The partitioning of the metals to the activated sludge biomass is accomplished by a physical-chemical process rather than by active biological transport, based on studies by Cheng et al (1975) who observed that the adsorption of metals to biomass was only slightly impeded in autoclaved sludge samples relative to fresh sludge. Nelson et al (1981) also compared adsorption of metals to fresh and autoclaved sludge samples, and found that in general there was no difference in adsorption of metals between live and dead biomass. An example of the results obtained by Nelson et al (1981) with zinc is shown in Figure 2.

Most literature references agree that the binding capacity of the activated sludge is due to exocellular polymers (Cheng et al, 1975; Bagby and Sherrard, 1981; Nelson et al, 1981). Brown and Lester (1982a) compared removals of metals by sludge biomass that was either untreated or extracted with solvent to remove the exocellular polymer. Metal removals were lower (i.e. adsorption capacities were lower) in the extracted samples than in the samples retaining the polymers, over a metal concentration range of 10 to 10,000 mg/L. The differences in adsorption between extracted and unextracted biomass samples were variable between metals, with cadmium showing little difference, and cobalt showing a great difference (Brown and Lester, 1982a). Among the chemical functional groups in the polymers that may be responsible for bonding the metals are phosphoryl, carboxyl, sulphydryl, and hydroxyl groups (Nelson et al, 1981).

In an investigation of adsorption of trace metals with a "dried stabilized" sludge, it was concluded that neither Freundlich or Langmuir adsorption models described the data, and that the removal mechanism was more similar to ion exchange than to adsorption (Roman-Seda, 1985). The sludge used was not comparable to the other studies in that it had been dried, sifted and sieved.

Metal uptake by the activated sludge is rapid. In one study, over 80 percent of copper and over 95 percent of lead was associated with the mixed liquor after 10 minutes of contact (Cheng et al, 1975). Nickel uptake was slower. The uptake of cadmium, zinc and mercury by activated sludge was also reported to be rapid by Neufeld and Herman (1975) although it was indicated that equilibrium was achieved within three hours. Nelson et al (1981) observed that uptake of cadmium, copper and zinc by activated sludge was rapid and essentially complete within one hour of contact. In another study, greater than 90 percent of the cadmium was adsorbed in 15 minutes, and 97 to 98 percent was adsorbed in three hours (Elenbogen et al, 1985).

Cadmium and nickel uptake by activated sludge proceeded in a rapid initial phase (less than 10 minutes), followed by a slower second phase that lasted for a number of hours in a study by Kodukula and Patterson (1984). Approximately 90 percent of the initial cadmium concentration and nearly 60 percent of the initial nickel concentration was adsorbed by the biomass in less than ten minutes.

Although the adsorption of metals to the activated sludge biomass is rapid, the binding capacity of the sludge is generally considered to be finite. It was estimated that saturation of the metal binding sites in the exocellular polymers of activated sludge occurred at concentrations of 10,000 ug/L for each of cadmium, cobalt and nickel (Brown and Lester, 1982a). Lawson et al (1984) observed also that the mixed liquor had a limited capacity to adsorb metals. Based on literature references, Rossin et al (1982) concluded that activated sludge biomass has a finite capacity to adsorb copper and nickel. Cheng et al (1975) noted that mixed liquor suspended solids had an upper limit for adsorption of metals.

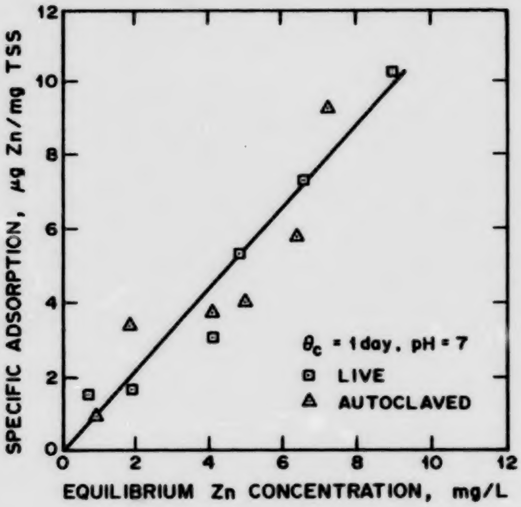

FIGURE 2—ZINC ADSORPTION ISOTHERMS COMPARING AUTOCLAVED AND LIVE SLUDGE BIOMASS (Nelson *et* *al*, 1981)

Among the chemical factors which influence the ability of the sludge biomass to adsorb metals is pH (Cheng et al, 1975). It was suggested that hydrogen ions compete with metallic cations for binding sites on the sludge biomass. An increase in pH, conversely, results in an increase in the number of free binding sites, permitting greater metal binding to the sludge. In continuing this line of investigation, high removal efficiencies (90 percent) for cadmium and nickel were achieved when the pH of the mixed liquor was above 8 (Kodukula and Patterson, 1984). When the pH declined to 7, however, nickel removal also declined to 60 percent while cadmium removal was still high. These results suggested that the lowest metal removals would be observed at low solids concentrations and low pH (Kodukula and Patterson, 1983). Nelson et al (1981) also concluded that pH is the most important factor governing metal adsorption by activated sludge, and that the optimum pH for removal of trace metals by activated sludge is greater than 8.0. It should be noted as well that the minimum solubility of most metals occurs when the pH exceeds 8.0. The effect of reduced metal solubility above pH 8.0 on adsorption to biomass was not indicated.

Several studies have investigated methods for improving metal accumulation by activated sludge through control of operating parameters such as solids retention time (SRT). In bench-scale studies, the metal adsorptive capacity of sludge was much higher at 3 d than 9 or 18 d (Brown and Lester, 1982b). Rossin et al (1982) reported that the maximum accumulation by mixed liquor solids occurred at a 9 d SRT for chromium, copper, nickel and lead, while the highest accumulation for cadmium was at a 4 d SRT, and for zinc at a 12 d SRT. The adsorptive capacity of metals by sludge biomass was higher at 5 d SRT than 1 d for cadmium, copper and zinc (Nelson et al, 1981). Manipulation of SRT was unable to control either cadmium accumulation in the activated sludge biomass or the effluent cadmium concentration of a full-scale plant (Elenbogen et al, 1985).

Nickel is a metal which frequently has a poor removal rate through water pollution control plants. Through the use of gel permeation chromatography, nickel in treatment plant effluents was found to be mainly associated with soluble organic ligands (Rossin et al, 1982). Nickel was not subject to precipitation like other metals at concentrations up to 10,000 ug/L, and also had less affinity for the exocellular polymers than cadmium (Brown and Lester, 1982a). Free uncomplexed nickel and soluble nickel forms were differentiated using ion exchange techniques (Neilsen et al, 1984). They determined that very little of the nickel in Edmonton Alberta wastewater was in the free uncomplexed form (only 6 percent), and that only this species was able to bind to the activated sludge flocs. Because soluble nickel comprised 50 to 65 percent of the total nickel, only 40 percent of the metal (i.e. the particulate form) would be removed by wastewater treatment and that removal would occur mainly in the primary clarifier. In concluding, it was suggested that when nickel concentrations increased and exceeded the complexing capacity of the wastewater, the removal of nickel by activated sludge would become more important (Neilsen et al, 1984).

Similar trends are probably true for other mostly soluble metals. Ninety-seven percent of the organics which complex copper in the effluent from an activated sludge plant was retained in the filtrate passing through a 0.45 um filter (Buckley, 1983). In a final effluent from a British wastewater treatment plant, 87 percent of manganese, 76 percent of cadmium and 67 percent of copper were found in filtrates with particle sizes of 0.4 um or less. Conversely, in the same study 77 percent of lead and 72 percent of iron were associated with particles of size 0.4 um or greater (Laxen and Harrison, 1981). The greater the fraction of metals passing through 0.4 um filters, the less probable would be the removal of the metals by sedimentation processes.

With respect to the relative importance of mechanisms, adsorption of metals to activated sludge is more important than precipitation for the removal of metals from settled wastewater (Brown and Lester, 1982a; Kodukula and Patterson, 1984).

4.3.2 Organics

The contribution of volatilization, biodegradation and biosorption as the mechanisms involved in the removal of organic contaminants from wastewater have been estimated by a number of researchers. The results are summarized in Table 97. The data were not all consistently reported in the literature. For example, Petrasek et al (1983b) reported only the removal of contaminants attributed to combined volatilization and stripping, and Klecka (1982) did not specify the removal due to biosorption of methylene chloride from activated sludge. Neither Shaul et al (1985) nor Games et al (1982) reported the importance of volatilization as a removal mechanism for azo dyes or a surfactant, respectively. Lurker et al (1982) reported only the removal of chlorinated hydrocarbons due to volatilization. Consequently, direct comparisons of removals attributed to specific mechanisms are not always possible.

There are, however, a number of observations which can be made as a result of the data summarized in Table 97. In general the relative removals due to the various mechanisms are fairly consistent in the studies of Kincannon et al (1983), Jones (1984), Wukasch et al (unpublished) and Lawson and Siegrist (1981). The main observations from these three studies are as follows:

(1) volatilization and/or biodegradation are the principal removal mechanisms for the compounds investigated;

(2) total removals of these compounds are high (i.e. the proportion of the initial compound remaining in the effluent is low, typically less than 5 percent; and

(3) biosorption is a relatively unimportant mechanism for removal of volatile organics, but is a significant removal mechanism for phthalates, and may be for other compounds such as PAHs.

The relative importance of the individual mechanisms for trace organic contaminant removal in activated sludge systems has also been addressed by the U.S. EPA (1986) and is reported in Table 97. In this report, the proportionate removals were not experimentally derived as in the work of Kincannon et al (1983), Jones (1984) or Wukasch et al (unpublished). Rather, the EPA (1986) first established the overall removal of a compound, and then estimated the proportion of the contaminant removed by volatilization based on EPA data. The proportion of the compound that was adsorbed to the biosolids was estimated from the 40 POTW study (EPA, 1982a) while the proportion biodegraded was calculated by difference. The EPA (1986) report is

TABLE 97. ESTIMATES OF RELATIVE IMPORTANCE OF REMOVAL MECHANISMS FOR SPECIFIC ORGANIC CONTAMINANTS

COMPOUND	PERCENT REMOVED BY				REFERENCE
	VOLATILIZATION	BIODEGRADATION	ADSORPTION	EFFLUENT	
Acrolein	0	99.9	0	0.1	(1)
Acrylonitrile	0	100	0	0	(1)
	0.08	99.8	0	0.1	(10)
Benzene	16	84	0	0.1	(1)
	16	84	0	<1	(2)
	24	69	2	5	(9a)
	72	16	2	10	(9u)
Bromoethane	86	10	0	5	(9a)
	90	5	0	5	(9u)
Carbon tetrachloride	72	6	13	10	(9a)
	77	0	11	15	(9u)
Chlorobenzene	20	80	0	<1	(2)
	<14	>86	0.002	<0.03	(3)
	27	50	15	10	(9a)
	45	32	15	10	(9u)
Ethyl acetate	7	93	0	0.1	(1)
Chloroform	63	25	2	10	(9a)
	72	6	2	20	(9u)
Dichlorodifluoromethane	90	5	0	5	(9a)
	90	5	0	5	(9u)
Ethyl benzene	22	78	0	<1	(2)
	24	66	6	5	(9a)
	72	13	6	10	(9u)
Methylene chloride	7	93	0	0.3	(1)
	8	82	-	10	(4)
o-Xylene	25	75	0	<1	(2)
Tetrachloroethylene	45	42	3	10	(9a)
	68	14	3	15	(9u)
Toluene	17	83	0	<1	(2)
	<40	>60	<0.01	<0.03	(3)
	24	45	27	5	(9a)
	72	0	25	10	(9u)
	1.2	98.7	0	0.1	(10)
Trichloroethylene	67	23	6	5	(9a)
	70	12	6	13	(9u)
Trichlorofluoromethane	76	19	0	5	(9a)
	81	9	0	10	(9u)
Vinyl chloride	86	8	2	5	(9a)
	90	3	2	5	(9u)
1,1-Dichloroethane	63	27	0	10	(9a)
	72	8	0	20	(9u)
1,1-Dichloroethylene	76	19	0	5	(9a)
	81	9	0	10	(9u)
1,1,1-Trichloroethane	98.6	0	0	1.4	(1)
	76	18	1	5	(9a)
	81	8	1	10	(9u)
1,1,2-Trichloroethane	40	40	0	20	(9a)
	20	5	0	75	(9u)

TABLE 97. ESTIMATES OF RELATIVE IMPORTANCE OF REMOVAL MECHANISMS FOR SPECIFIC ORGANIC CONTAMINANTS (cont'd)

COMPOUND	PERCENT REMOVED BY				REFERENCE
	VOLATILIZATION	BIODEGRADATION	ADSORPTION	EFFLUENT	
1,1,2,2-Tetrachloroethane	94.5	0	0	5.5	(1)
	36	50	4	10	(9a)
	15	9	1	75	(9u)
1,2-Dichloroethane	97.6	0	1	1.4	(1)
	45	41	5	10	(9a)
	45	3	3	50	(9u)
	10.4	79	0	11.6	(10)
1,2-trans-Dichloroethylene	63	0	49	10	(9a)
	72	0	43	20	(9u)
1,2-Dichloropropane	89	a	a	1	(1)
	45	45	0	10	(9a)
	63	7	0	30	(9u)
Nitrobenzene	0	97.8	0	2.2	(1)
	<1	98	0	2	(2)
1,2-Dichlorobenzene	22	78	0	0	(1)
	59	35	0	6	(2)
	45	14	32	10	(9a)
	78	0	30	13	(9u)
	0	99.9	0.01	0.1	(10)
1,3-Dichlorobenzene	45	42	3	10	(9a)
	78	6	3	13	(9u)
1,4-Dichlorobenzene	45	23	23	10	(9a)
	78	0	22	13	(9u)
1,2,4-Trichlorobenzene	43	35	8	15	(9a)
	51	26	8	15	(9u)
	90	0	<1	10	(2)
Isophorone	0	99.8	0.003	0.2	(10)
Dimethyl phthalate	<0.10	>99.9	<0.01	<0.03	(3)
	*	96*	-	-	(5)
	0	95	0	5	(9a)
	0	65	0	35	(9u)
Diethyl phthalate	*	81*	-	-	(5)
	0	89	1	10	(9a)
	0	74	1	25	(9u)
Di-n-butyl phthalate	*	44*	-	-	(5)
	0	70	20	10	(9a)
	0	70	20	10	(9u)
Butylbenzyl phthalate	*	0*	-	-	(5)
	0	52	43	5	(9a)
	0	50	41	10	(9u)
Bis(2-ethylhexyl) phthalate	*	0*	-	-	(5)
	<0.01	71	25.7	3.3	(3)
	0	24	66	10	(9a)
	0	24	66	10	(9u)
Di-n-Octyl phthalate	*	0*	-	-	(5)
	0	83	7	10	(9a)
	0	83	7	10	(9b)
	0	64	1.3	34.7	(10)
Acenaphthene	*	52*	-	-	(5)

TABLE 97. ESTIMATES OF RELATIVE IMPORTANCE OF REMOVAL MECHANISMS FOR SPECIFIC ORGANIC CONTAMINANTS (cont'd)

COMPOUND	PERCENT REMOVED BY				REFERENCE
	VOLATILIZATION	BIODEGRADATION	ADSORPTION	EFFLUENT	
Anthracene	*	25*	-	-	(5)
	0	43	52	5	(9a)
	0	41	50	10	(9u)
Benzo(a)anthracene	*	131*	-	-	(5)
Chrysene	*	9*	-	-	(5)
Fluoranthene	*	0*	-	-	(5)
Fluorene	*	44*	-	-	(5)
Naphthalene	<53	>47	0.20	<0.12	(3)
	*	77*	-	-	(5)
	0	99.5	0.04	0.06	(10)
	29	40	27	5	(9a)
	23	32	21	25	(9u)
Phenanthrene	*	37*	-	-	(5)
Pyrene	*	0*	-	-	(5)
Phenol	0	100	0	0	(1)
	0.03	99.7	0.002	0.26	(10)
	*	90*	-	-	(5)
	0	81	14	5	(9a)
	0	72	13	15	(9u)
2,4-Dichlorophenol	0	95.2	0	4.8	(1)
Pentachlorophenol	0.03	99.3	0.16	0.57	(3)
	*	0*	-	-	(5)
	0	78	17	5	(9a)
	0	21	5	75	(9u)
2,4-Dimethylphenol	*	98*	-	-	(5)
2,4-Dinitrophenol	0	99	1	<0.7	(1)
p-Chloro-m-cresol	<0.01	98.4	1.52	0.06	(3)
Dinitro-o-cresol	0.38	95.0	0.08	4.5	(3)
Lindane (gamma-BHC)	0	0	7	93	(2)
	*	25*	-	-	(5)
Heptachlor	*	25*	-	-	(5)
Toxaphene	*	40*	-	-	(5)
Aroclor 1254	*	0*	-	-	(5)
Azo Dye	-	74-81	9-15	10-11	(6)
Hexachlorobicycloheptene	52	-	-	-	(7)
Heptachlorobicycloheptene	21	-	-	-	(7)
Chlordane	0.6	-	-	-	(7)
Octadecyltrimethyl Ammonium Chloride	-	63-89	11-35	2-4	(8)

Notes:
1) Percent removals from Ref. 9 do not always total 100% (e.g. toluene, 1,2-t-dichloroethylene, 1,2-dichlorobenzene).
2) a = No biodegradation observed.
3) * = Removal due to biodegradation plus volatilization.
4) In Ref. 9, a = acclimated sludge
u = unacclimated sludge
5) - Means mechanism not specified.

References:
1) Kincannon *et al*, 1983
2) Jones, 1984
3) Wukasch *et al*, Undated
4) Klecka, 1982
5) Petrasek *et al*, 1983b
6) Shaul *et al*, 1985
7) Lurker *et al*, 1982
8) Games *et al*, 1982
9) EPA, 1986
10) Lawson & Siegrist, 1981

useful because it differentiates between acclimated and unacclimated biomass. One drawback, however, is that this report stipulates a maximum total removal of 95% for any contaminant, while other investigations indicate that total removals may be as high as 99.9 percent.

Another shortcoming of this EPA report is evident for compounds such as toluene, trans-1,2-dichloroethylene, and 1,2- and 1,4-dichlorobenzene. The total removal for these contaminants in unacclimated systems is significantly higher than 100 percent, in spite of predicted removals of 87 to 95 percent. The importance of volatilization as a removal mechanism in unacclimated systems is considered high for compounds such as benzene, toluene and ethyl benzene, whereas in acclimated systems, biodegradation of the contaminants is the primary removal mechanism. Adsorption to biosolids was assigned a greater role in the EPA (1986) report than in other studies (e.g. Kincannon et al, 1983; Jones, 1984; Wukasch et al, unpublished; Lawson and Siegrist, 1981), particularly for compounds such as chlorobenzene, toluene, 1,2-dichlorobenzene, naphthalene and phenol.

There is considerable variation in the importance attached to various mechanisms for a few compounds reported by different authors. Estimates of the removal of 1,2-dichlorobenzene due to biodegradation range from 99.4 percent of the influent (Lawson and Siegrist, 1981) to 35 percent (Jones, 1984) to 0 to 14 percent (EPA, 1986) depending on whether or not the activated sludge is acclimated. Wukasch et al (unpublished) estimated that 71 percent of the influent level of bis(2-ethylhexyl) phthalate was removed by biodegradation and 26 percent by biosorption. Conversely, EPA (1986) indicated that biodegradation and biosorption accounted for 24 and 66 percent, respectively. The study by Kincannon et al (1983) attributed most of the removal of 1,2-dichloroethane and 1,1,2,2-tetrachloroethane to volatilization, while Lawson and Siegrist (1981) attributed 79 percent of the removal of 1,2-dichloroethane to biodegradation and only 10 percent to volatilization. In the EPA (1986) report, the removal of these compounds was suggested to be a combination of volatilization and biodegradation in acclimated systems, or loss of the contaminant in the effluent for unacclimated systems. Petrasek et al (1983b) reported that neither volatilization nor biodegradation resulted in reductions of butyl benzyl phthalate, bis(2-ethylhexyl) phthalate and di-n-octyl phthalate, and pentachlorophenol. The results of Wukasch et al (unpublished) and the EPA (1986) indicate that biodegradation in particular may play a more important role as a removal mechanism than the results of Petrasek et al (1983b) would indicate.

In summary, the data for Table 97 indicate the purgeable compounds are removed primarily by volatilization or biodegradation, depending on the degree of acclimation of the activated sludge. Adsorption does not play a significant role in removal of purgeables with the possible exception of 1,2-trans-dichloroethylene. In the base/neutral extractable group, the chlorinated benzenes are generally removed by volatilization and biodegradation. The phthalate esters are not removed by volatilization, but by a combination of biodegradation and biosorption. Removal mechanisms for the PAH group are not well characterized. This group of contaminants does appear to be biodegraded to some extent but volatilization does not appear to play a significant role with the exception of the lower molecular weight compound naphthalene.

Biosorption may also have a role in the removal of PAHs [e.g. approximately 50 percent removal of anthracene by biosorption (EPA, 1986)], but this removal mechanism is not well defined for PAHs or pesticides. The phenolic compounds do not appear to be volatilized nor sorbed to biosolids to any extent; rather, biodegradation appears to be the major removal mechanism. Pesticide and PCB compounds have been poorly characterized with respect to removal mechanisms. At best, it appears from the data in Table 97 that the compounds are not biodegraded or volatilized to a great degree.

A number of additional studies have attempted to define the removal mechanisms for organic compounds in activated sludge systems. Little removal of organochlorine pesticide occurred in a large pilot-scale facility, but a certain amount of biotransformation did occur (Saleh et al, 1980). For example, DDT was degraded to DDD or DDE, and aldrin to dieldrin. The phenoxy herbicide 2,4-D was partially transformed to short chain alkyl esters. Generally poor removal of chlorinated phenoxy herbicides by wastewater treatment was observed in the U.K. (Hill et al, 1986). Neither adsorption nor biodegradation were considered significant removal mechanisms, and the majority (>80 percent) of the compounds passed untreated through the system. Very little Lindane (gamma-BHC) was removed by volatilization from bench-scale activated sludge units, and adsorption to biosolids appears to be a more important removal mechanism (Weber et al, 1983).

Volatilization was found to be the most important mechanism for removal of methylene chloride from unacclimated systems, whereas for acclimated activated sludge, biodegradation is the primary removal mechanism (Klecka, 1982). The cationic surfactant ditallow-dimethyl ammonium chloride was removed by both biodegradation and a precipitation/sorption mechanism in lab-scale activated units. Kinetic studies indicated that sorption to the biomass was faster than degradation, and that sorption was perhaps the first step in the overall removal (Sullivan, 1983).

In an investigation of contaminant removal during biological treatment of coke plant effluents, the primary removal mechanism was found to be sorption to biomass (Ganczarczyk, 1980). The concentrations studied were approximately three orders of magnitude higher than in municipal wastewaters.

In pilot-scale activated sludge units, approximately 75-80 percent of the total removal was of an azo dye was attributed to biodegradation, and 10-15 percent to biosorption (Shaul et al, 1985). The adsorption removal rate was based on isotherms developed using lyophilized heat dried activated sludge.

In comparing removals of chloroform and hexachlorobicycloheptene (Hex-BCH) from a bench-scale activated sludge unit, the chloroform volatilization rate was unaffected by solids and depended only on the aeration rate, whereas the Hex-BCH stripping rate was reduced by solids (Lurker et al, 1984. It was concluded that the difference was explained by chloroform being stripped from the liquid phase while Hex-BCH was stripped from the solid phase, i.e. it was adsorbed to the biosolids.

In a study using a pilot-scale rotating biological contactor, naphthalene was removed by initial adsorption to the biofilm, followed by biodegradation (Glaze et al, 1985).

4.4 Mathematical Models of Removal Mechanisms for Trace Contaminants

4.4.1 Models for Removal of Metals

A comprehensive attempt at establishing a model for removal of metals by activated sludge was prepared by Nelson *et al* (1981). In developing the model it was assumed that:

(i) Equilibrium conditions existed

(ii) Complexing ligand concentrations > metal concentration

Actual mathematical development of the model is described in detail by Nelson *et al* (1981), and the reader is directed to the text of this paper for step-by-step development. In summary, expressions were developed which were of the form of a Langmuir adsorption isotherm, a conditional metal-ligand equilibrium and a conditional equilibrium between uncomplexed metal and a bacterial surface. As a result of the modelling, expressions were derived that would predict the distribution of metal as uncomplexed, or complexed, and soluble or adsorbed forms.

Based on concentration of ligands in the synthetic wastewater either measured or estimated, specification-distribution diagrams were derived for trace metals under various experimental conditions (Nelson *et al*, 1981). Figures 3 and 4 depict these diagrams for cadmium and copper as a function of pH, respectively. The figures show that a substantial fraction of cadmium is in the free uncomplexed form at pH = 7.0, while at the same pH little free uncomplexed copper exists.

The model of Nelson *et al* (1981) is conditional upon experimental conditions such as pH, and a modification of the adsorption portion of the model to include pH effects has been proposed (Martin *et al*, 1985). The modification included a pH term (i.e. hydrogen ion concentration) in the development of the conditional equilbrium adsorption constant, which is determined by experimental isotherms at specific pH values. Using the cadmium data of Nelson *et al* (1981), the ability of the revised model to predict adsorption of the metal to biomass was demonstrated (Martin *et al*, 1985). The results of this testing are depicted in Figure 5.

From the experimentally developed isotherms, the slope (conditional equilibrium adsorption constant) and intercept (product of conditional equilibrium stability constant and number of surface site per unit mass of solids) can be calculated. The distribution of metals among species and surfaces according to the model of Nelson et al (1981) can then be determined.

Empirical models to predict the proportion of solids bound metal relative to the total metal concentration have also been prepared (Patterson and Kodukula, 1984). An initial empirical model developed was of the form:

$$M_T/M_S = A + B/VSS \qquad (1)$$

where:
M_T = Total metal concentration
M_S = Solids-associated metal concentration
VSS = Volatile suspended solids concentration
A = Empirical constant dimensionless
B = Empirical constant, mg/L

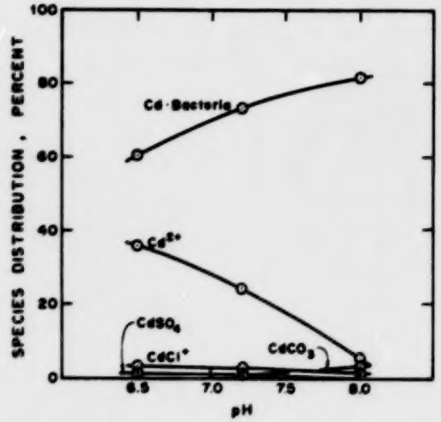

FIGURE 3—SPECIATION-DISTRIBUTION DIAGRAM FOR CADMIUM AS FUNCTION OF pH (Nelson _et al_, 1981)

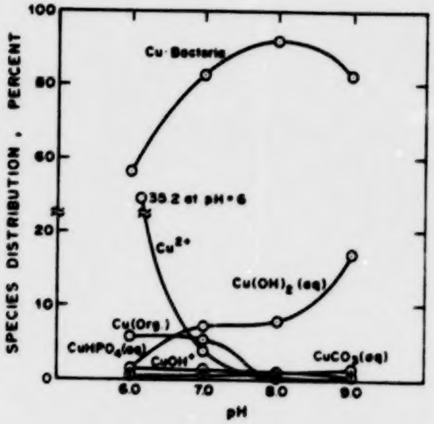

FIGURE 4—SPECIATION-DISTRIBUTION DIAGRAM FOR COPPER AS FUNCTION OF pH (Nelson _et al_, 1981)

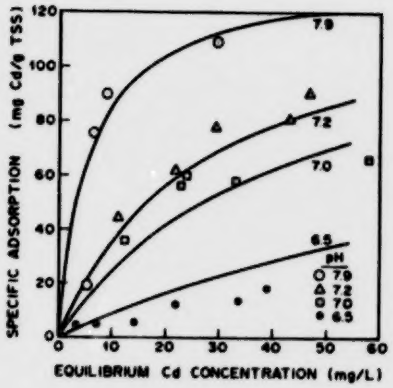

FIGURE 5—MEASURED (symbols) AND PREDICTED (lines) CADMIUM ADSORPTION TO SLUDGE BIOMASS AT DIFFERENT pH VALUES (Martin _et al_, 1985)

Empirical constants were developed by linear regression for raw wastewater, primary effluent, mixed liquor and secondary effluent for a series of 8 trace metals. The model had the most success in fitting data in the raw wastewater and mixed liquor streams (i.e. high solids wastewater streams). The worst fit was observed for nickel in primary effluent, with an r^2 value of 0.560.

In refining this empirical model, a more simplistic relationship resulted in higher correlation (Patterson and Kodukula, 1984). This second model was

$$M_T = pM_S + q \qquad (2)$$

where:
p = Empirical constant dimensionless
q = Empirical constant, mg/L

The calculated empirical constants and correlation coefficient (r^2) are reported in Table 98. With this model, all r^2 values exceeded 0.9. The model indicates that the empirical constant q is the soluble metal concentration. The authors noted that the model was only valid over the range of experimental conditions from which it was developed, and so is less general than the model developed by Nelson et al (1981).

TABLE 98. REGRESSION CONSTANTS AND CORRELATION COEFFICIENTS FOR THE EMPIRICAL METALS DISTRIBUTION MODEL II (PATTERSON AND KODUKULA, 1984)

METAL	CONSTANT	PROCESS LIQUID			
		RAW WASTEWATER	PRIMARY EFFLUENT	MIXED LIQUOR	SECONDARY EFFLUENT
Aluminum	p	0.953	0.890	1.003	0.955
	q	107	122	38	100
	r^2	0.975	0.961	0.999	0.961
Cadmium	p	1.045	1.089	1.035	1.022
	q	11	9	1	12
	r^2	0.963	0.944	0.994	0.947
Chromium	p	1.002	1.004	1.001	1.007
	q	4	3	2	3
	r^2	0.999	0.999	0.999	0.999
Copper	p	1.016	1.018	1.001	1.001
	q	12	7	9	12
	r^2	0.998	0.998	0.999	0.998
Iron	p	0.997	0.992	0.999	0.945
	q	173	107	106	108
	r^2	0.993	0.985	0.999	0.983
Lead	p	1.036	1.024	1.007	1.137
	q	15	13	10	11
	r^2	0.976	0.981	0.999	0.953
Nickel	p	1.033	1.090	1.019	1.300
	q	276	2456	172	106
	r^2	0.964	0.909	0.999	0.913
Zinc	p	0.928	0.961	0.997	0.943
	q	137	96	108	90
	r^2	0.981	0.992	0.999	0.988

Prediction of metal concentrations in return activated sludges, based on a concentration factor calculated from influent and effluent concentrations and reactor operating conditions (e.g. SRT, HRT, MLVSS), was proposed by Melcer and Bridle (1985). the concentration factor CF was defined by the relationship:

$$CF = C_s / (C_o - C_e) \tag{3}$$

where:
C_s = Sludge contaminant concentration (mg/kg)
C_o = Influent contaminant concentration (mg/L)
C_e = Effluent contaminant concentration (mg/L)

By several substitutions, it was also shown that the Cf could be expressed as:

$$CF = (SRT \cdot 10^6) / (HRT \cdot X) \tag{4}$$

where:
SRT = Solids retention time (days)
HRT = Hydraulic retention time (days)
X = Mixed liquor volatile suspended solids (mg/L)

The data of Petrasek et al (1983c) were used to confirm the model. Operating data were substituted in Equation (4) to derive a concentration factor of 9,426. The Cf was then substituted into Equation (3), and, knowing the influent and effluent concentrations, a predicted concentration in the return activated sludge could be calculated. Predicted and observed sludge concentrations are summarized in Table 99. The ratios of predicted and observed concentrations ranged between 0.64 for chromium and 6.23 for cadmium, indicating that the predicted concentrations were well within an order of magnitude of the observed values.

TABLE 99. COMPARISON OF PREDICTED AND MEASURED RETURN ACTIVATED SLUDGE METAL CONCENTRATIONS (MELCER AND BRIDLE, 1985)

METAL	RAS CONCENTRATION (mg/kg)		RATIO PREDICTED/ MEASURED
	PREDICTED	MEASURED	
Cd	86	13.8	6.23
Cr	1,602	2,474	0.64
Cu	3,865	2,817	1.37
Ni	848	699	1.21
Pb	4,430	2,368	1.87
Zn	7,729	2,977	2.60

4.4.2 Models for Removal of Organics

4.4.2.1 Stripping (Volatilization)

Volatilization may be an important mechanism for the removal of low molecular weight organics from wastewater aeration basins, particularly in activated sludge systems which are not acclimated to the contaminant (EPA, 1986). For most volatile organics, the stripping rate is controlled by equilibrium of the compound between the liquid phase and an air bubble. This implies that the compounds obey Henry's Law. Equilibrium is governed by the liquid mass transfer resistance. Except for a few highly volatile compounds such as vinyl chloride, the air bubble is saturated with the organics in the water. The concentration of the more highly volatile organics, conversely, is kinetically controlled, and the liquid phase resistance and bubble residence time in the liquid determine the gas phase concentration (Allen et al, 1986).

One model for the removal of organics from wastewater by volatilization was derived by Blackburn et al (1985). A stripping mass removal equation was assumed to be first order and was of the form:

$$V \left[\frac{dC_{ae}^{st}}{dt} \right] = V\, K_a{}^{st} a\, C_{ae} \qquad (5)$$

where:

C_{ae}^{st} = Equilibrium contaminant concentration in aqueous phase during stripping, mg/L

V = Reactor volume, L

t = Time, day

$K_a{}^{st}a$ = Stripping rate constant, day^{-1}

The stripping rate constant was derived from an empirical relationship involving reactor volume and Henry's Law Constant. Tests in tapwater were conducted with phenol, methyl ethyl ketone, toluene and 1,4-dichlorobenzene. From these tests runs, the stripping rate constant was determined to be:

$$K_a{}^{st}a = \frac{Q_{air}}{V} \cdot 6.18 \times 10^{-5}\, H_c{}^{1.045} \qquad (6)$$

where:

Q_{air} = Airflow rate, L/d

$K_a{}^{st}a$ = Stripping rate constant, day^{-1}

H_c = Henry's Law Constant (torr·L)/(g-mole)

This approach was also adopted by Moos et al (1983) to determine the relative importance of volatilization for the removal of pentachlorophenol (PCP) from an activated sludge system.

A different approach to modelling the removal of volatile organics in aeration basins by stripping has been reported (Roberts et al, 1984). Mass transfer rates of specific organic contaminants from water were determined based on the estimated oxygen mass transfer coefficients and proportionality constants determined by laboratory experiments, i.e.

$$(K_La)_i = \beta_i\, (K_La)O_2 \qquad (7)$$

where:

$(K_La)_i$ = Overall mass transfer rate constant of contaminant i (s^{-1})

$(K_La)O_2$ = Overall mass transfer rate constant for dissolved oxygen (s^{-1})

β_i = Mass transfer rate proportionality constant for contaminant i

The estimated mass transfer rate constants for the contaminants were next substituted into mass transfer equations to determine the removal rates of the contaminants. Concerns about this method, principally with respect to fine bubble aeration systems have been raised (Allen *et al*, 1986). It has been suggested that equilibrium can be assumed between the purgeable organics and the air bubble, but this assumption may not be valid for oxygen, which is considered a more volatile compound than the organics.

Roberts *et al* (1984) then established a model for organic contaminant removal by stripping in bubble aeration systems. Assumptions used in this model were:

(i) the overall mass transfer rate constant K_La is constant over the depth of the aeration tank;

(ii) equilibrium at the bubble/liquid interface obeys Henry's law;

(iii) air flowrate and temperature are constant;

(iv) the liquid phase is well-mixed.

Roberts *et al* (1981) first utilized the fractional saturation of an air bubble by an organic contaminant i, which can be expressed as follows:

$$\frac{C_{G,E}}{C_G^*} = 1 - e^{-\phi i} \qquad (8)$$

where:

$C_{G,E}$ = Contaminant i concentration in exiting gas bubbles

C_G^* = C_LH_C = gas phase concentration (g/m^3) in equilibrium with the liquid phase

ϕi = Saturation parameter

The saturation parameter for contaminant i is defined as

$$\phi_i = \frac{(K_La)_iV}{(H_C)_iQ_G} \qquad (9)$$

where:

V = Reactor volume, m^3

$(H_C)_i$ = Henry's Law constant, dimensionless

Q_G = Air flowrate, m^3/s

The fraction of volatile organic contaminant removed by bubble aeration can finally be expressed as (Roberts *et al*, 1984):

$$1 - \frac{C_{L,E}}{C_{L,I}} = 1 - [1 + (Q_G/Q_L)(H_C)_i\ (1-e^{-\phi i})]^{-1} \qquad (10)$$

For mechanical aeration, an expression, based on a mass balance equation, which relates the influent and effluent concentrations of contaminant i was similarly derived (Roberts *et al*, 1984):

$$\frac{C_{L,E}}{C_{L,I}} = [1 + \theta \, K_L a]^{-1} \qquad (11)$$

where:

$C_{L,E}$ = Effluent concentration of contaminant i, g/m^3
$C_{L,I}$ = Influent concentration of contaminant i, g/m^3
θ = Hydraulic retention time, d

The fractional removal of the contaminant, assuming proportionality with the oxygen mass transfer rate, is:

$$1 - \frac{C_{L,E}}{C_{L,I}} = 1 - [1 - \theta \beta_i \, (K_L a)_{O_2}]^{-1} \qquad (12)$$

Roberts et al (1984) then specified conditions of operation to calculate the fractional removals. The calculations provided several interesting observations:

(1) Surface aeration releases more volatile organics to the atmosphere than bubble aeration.

(2) In bubble aeration, the removal efficiency by stripping declines as the Henry's law constant declines.

(3) In bubble aeration, the transfer efficiency of organic contaminants decreases with increasing oxygen transfer efficiency, when the overall oxygen transfer requirement is maintained constant.

For the compounds investigated (dichlorodifluoromethane, carbon tetrachloride, tetrachloroethylene, trichloroethylene and chloroform), removal by volatilization in surface aeration was calculated to be 84 to 86 percent. Excluding dichlorodifluoromethane, removal range in bubble aeration for the volatiles examined was 35 to 78 percent. This model has not yet been validated by field testing.

Blackburn et al (1985) suggest that this Equation (11) with appropriate substitution and mathematical manipulation is essentially of the same form as their Equation (6) when the saturation parameter Φ, is greater than 5 (i.e. when the gas phase is saturated). In bubble aeration, the gas bubbles become saturated when compounds have Henry's Law constants of approximately 1 or less (Roberts et al, 1984).

Jones (1984) has also developed a model for the removal of trace organics from activated sludge systems by volatilization. Based on a mass balance equation for a trace organic compound in the aqueous phase,

$$V \frac{(dC)}{(dt)} = QC_i - QC_e - k_v C_e V \qquad (13)$$

where:

V = Reactor volume
C_i = Influent concentration
C_e = Effluent concentration
Q = Flowrate
k_v = Stripping rate constant

The steady state effluent concentration of the organic compound is

$$C_e = C_i / (1 + k_v \bar{t}) \qquad (14)$$

where $\bar{t}$ is the mean hydraulic retention time. This is of the same form as the expression derived by Roberts et al (1984) for mechanical aeration (Equ. 12).

Through a series of experimental tests which stripped specific compounds from clean water, the stripping rate constant for the organics by linear regression techniques were calculated (Jones, 1984). The results are summarized in Table 100. Correlation coefficients obtained for the regression of the natural logarithm of the aqueous concentration versus time were high. Then, to include the effect of aeration rate on the stripping rate constant, Jones (1984) described the relationship,

$$k_v = k_{v,o} + Q_a L \qquad (15)$$

where:

$k_{v,o}$ = Empirical constant, min^{-1}
L = Empirical constant, L^{-1}
Q_a = Aeration rate, L/min

TABLE 100. TRACE ORGANIC VOLATILIZATION RATE COEFFICIENTS FROM AIR STRIPPING STUDIES IN WATER (JONES, 1984)

COMPOUND	k_v (min^{-1})	CORR. COEFF. (r)
Ethyl benzene	0.0874	0.997
Toluene	0.0765	1.000
Benzene	0.0754	1.000
o-Xylene	0.0615	0.999
Chlorobenzene	0.0493	0.999
1,2-Dichlorobenzene	0.0240	0.997
1,2,4-Trichlobenzene	0.0236	0.991

The values of the empirical constants derived by Jones are found in Table 101. Because the intercept value $k_{v,o}$ is very close to zero, Equation (15) reduces to

$$k_v = Q_a L \qquad (16)$$

which is of identical form with Equation (6) derived by Blackburn et al (1985.)

TABLE 101. VOLATILIZATION PARAMETERS RELATING STRIPPING RATE CONSTANT TO AIR FLOWRATE (JONES, 1984)

COMPOUND	k_{vo} (min^{-1})	L (L^{-1})	CORR. COEFF. (r)
Benzene	0.0012	0.0183	0.999
Toluene	0.0023	0.0188	0.999
Ethyl benzene	0.0027	0.0205	0.999
o-Xylene	0	0.0148	0.999
Chlorobenzene	0	0.0124	1.000
1,2-Dichlorobenzene	0	0.0064	0.993
1,2,4-Trichlorobenzene	0	0.0063	0.992

By similar mass balance equations and steady-state assumptions, derived an expression for the concentration of a trace organic contaminant in the off-gas from the reactor was derived (Jones, 1984):

$$C_g = \frac{C_e V}{Q_g} (k_{v,o} + Q_a L) \qquad (16)$$

where:

C_g = Off-gas concentration of contaminant, mg/L

Q_g = Off-gas flowrate, L/min

In pure water testing with specific organic compounds, the predictive equations were successful in estimating the concentration in aqueous effluent and off-gas, as shown in Table 102.

TABLE 102. PREDICTED EFFLUENT AND OFF-GAS CONCENTRATIONS FROM BIOREACTORS IN CLEAN WATER (JONES, 1984)

COMPOUND	INFLUENT (ug/L)	MEASURED EFFLUENT (ug/L)	PREDICTED EFFLUENT (ug/L)	MEASURED OFF-GAS (ng/L)	PREDICTED OFF-GAS (ng/L)
Benzene	120.3	4.6	4.5	846	835
Toluene	121.9	4.5	4.1	784	786
Ethyl benzene	112.0	3.5	3.7	758	787
o-Xylene	111.5	5.2	5.4	796	764
Chlorobenzene	130.9	6.8	6.7	790	828
1,2-Dichlorobenzene	105.2	10.8	11.0	691	706
1,2,4-Trichlorobenzene	117.7	12.2	12.2	765	772

In summary, the models developed for volatilization are based on assumed equilibrium conditions between the liquid phase and gas bubble in diffused air systems (i.e. they obey Henry's Law). Jones (1984) established stripping rate constants based on empirical models derived from tests with organic compounds dissolved in pure water, with subsequent verification by additional testing. A similar approach was taken by Blackburn *et al* (1985), who separated the equilibrium constant between liquids and gases (i.e. Henry's Law constant) from the stripping rate expression. The empirical constants, also developed in tests using clean water, were also verified by additional laboratory testing. It was shown, however, that substances such as salts, oils, surfactants, biomass and an industrial waste, in general tended to reduce the stripping rate (Blackburn *et al*, 1985).

A different approach estimated the transfer rate of an organic contaminant from the oxygen transfer rate using a laboratory derived proportionately constant (Roberts *et al*, 1984).

Of these models, only Blackburn *et al* (1985) attempted to evaluate the stripping rate of organics in the presence of biomass which had been inactivated. Whereas Blackburn *et al* (1985) indicated that biomass reduced stripping rates, laboratory experiments by Dobbs and Rao (1986) suggest that if initial adsorption by biomass is disregarded in batch tests, the stripping rates of organic contaminants over a wide range of volatility are nearly identical with or without mixed liquor solids.

4.4.2.2 Biosorption

Adsorption of organic contaminants to mixed liquor solids may be an important mechanism for hydrophobic compounds. For evaluation of the biosorption potential of activated sludge, it is necessary to eliminate any contributions of volatilization or biodegradation to the overall removal efficiency. Reactors with zero headspace to eliminate any volatilization effects, and lyophilized (freeze-dried) activated sludge as the inactive biomass were used in one study (Blackburn et al, 1985). Alternative methods of inactivation, including gamma irradiation and treatment with formaldehyde, were found to be less satisfactory. A minimum drying time of 3 hr at 105°C following lyophilization was selected as the optimum procedure. Upon rehydration, the lyophilized biomass resembled live biomass in both flocculating and settling properties, but no further elaboration was provided (Blackburn et al, 1985).

In establishing a model for biosorption, Blackburn et al (1985) assumed an equilibrium relationship.

$$C_s = K_{ba} \cdot C_{ae} \tag{18}$$

where:

C_s = Contaminant loading on sludge solids, mg/g
C_{ae} = Contaminant aqueous phase concentration, mg/L
K_{ba} = Biosorption distribution constant, L/g

Using laboratory data and linear regression techniques, a relationship was established between the biosorption distribution coefficient K_{ba} and the octanol/water partition coefficient K_{ow}. On the assumption that the lipids in the biomass are responsible for the sorption of the organic compounds, the following relationship was proposed:

$$K_{ba} = \frac{K_{ow} f_L}{P_L} \tag{19}$$

where:

f_L = Lipid weight fraction of the biomass (0.2 assumed)
P_L = Density of lipids, g/L

The validity of this model was tested with phenol, pentachlorophenol and 1,4-dichlorobenzene (Blackburn et al, 1985). At low contaminant concentrations, good agreement between predicted and observed distribution constants was observed. At high concentrations of 1,4-dichlorobenzene, the observed values of the biosorption distribution constant were considerably lower than the predicted values. Unfortunately, high levels of phenol and PCP were not tested under the same conditions.

The importance of biosorption in contaminant removal from activated sludge was investigated in another study (Jones, 1984). This methodology also minimized the possibility of volatilization of contaminants. Unacclimated viable mixed liquor biomass was used for the sorption studies rather than inactivated biomass, and so biodegradation could not be completely discounted. Three compounds were investigated: gamma-BHC (Lindane), 1,2-dichlorobenzene and 1,2,4-trichlorobenzene. Recovery tests for the compounds under investigation suggested that both

Lindane and 1,2,4-trichlorobenzene underwent reversible adsorption to the biomass. No results were reported for 1,2-dichlorobenzene. The 1,2,4-trichlorobenzene was sorbed to a greater extent than Lindane.

For modelling purposes, Jones (1984) considered adsorption in terms of the Freundlich isotherm

$$q_e = kC_e^{1/n} \qquad (20)$$

where:

q_e = Amount of contaminant adsorbed per mass of biosolids, mg/mg MLSS

C_e = Equilibrium aqueous phase concentration, mg/L

$K, 1/n$ = Freundlich isotherm constants

An equilibrium expression for partitioning of the organic compounds between the solids and the aqueous phase was next considered:

$$q_e = K_B C_e \qquad (21)$$

where:

K_B = Partitioning (bioconcentration) constant, L/mg MLSS

which is identical with Equation (18) of Blackburn et al (1985). The Freundlich isotherm reduces to Equation (21) when n=1, which occurs frequently at low contaminant concentrations (Jones, 1984). Both Equations (20) and (21) resulted in high correlation coefficients of equal value when experimental data were subjected to linear regression analysis. Next, the octanol/water partition coefficient was related to the bioconcentration constant using the expression of MacKay (1982):

$$K_B = 0.048K_{ow} \qquad (22)$$

The validation of this model was carried out by comparing the calculated bioconcentration factors from other studies (principally with fish) with the bioconcentration factors measured using the activated sludge biomass (Jones, 1984). Agreement was considered good.

Unacclimated sludge was also used to test the biosorption properties of pentachlorophenol (Moos et al, 1983). The ideal procedure of stopping sludge metabolism was considered so severe that the sorptive properties of the biomass would probably be altered. The approaches of Moos et al (1983) and Jones (1984) appear identical. Although the isotherm resulting from the tests of Moos et al (1983) did not fit either the Freundlich or Langmuir adsorption models, it was determined that biosorption was responsible for less than one percent of PCP removed in activated sludge.

Biosorption may be of greater importance as a removal mechanism when the soluble COD to contaminant ratio is high. This results in greater cell synthesis and requires higher sludge wasting rates (i.e. low SRT). PCP adsorbed to the sludge biomass would then be eliminated from the system at a higher rate.

Biosorption of 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane by inactivated mixed liquor biomass was shown to be described mathematically by a modified Freundlich isotherm

(Tsezos and Seto, 1986). the Freundlich equation incorporated a term for that portion of the chloroethane concentration that was resistant to biosorption. The more hydrophobic tetrachloroethane was sorbed to the biomass to a greater extent than the more water-soluble trichloroethane. This observation was consistent with greater biosorption of the compound with the higher octanol/water partition coefficient. Although biosorption of hydrophobic compounds is considered to increase as the lipid content of the biomass increses, Tsezos and Seto (1986) found that, with the activated sludge biomass inactivated by drying, lipid content was not the determining factor for biosorption of organics.

Adsorption of the pesticides lindane, diazinon and pentachlorophenol, and the PCB 2-chlorobiphenyl by inactivated microbial biomass was found to be described by a Freundlich isotherm (Bell and Tsezos, 1987). Adsorption of these pesticide/PCB compounds was reversible, suggesting that physical adsorption was responsible for removal of the compounds from wastewater. Malathion, another pesticide investigated, was highly adsorbed in an irreversible manner, possibly due to biodegradation. The results of Bell and Tsezos suggest that under appropriate conditions some contaminants can desorb from biomass, causing potential ground or surface water problems when sludges are land-spread or landfilled.

A methodology predicting trace organic contaminant concentrations in return activated sludge, makes use of concentration factors as discussed in Section 4.4.1 (Melcer and Bridle, 1985). Predicted organic concentrations were within an order of magnitude of observed concentrations for seven of ten compounds (Table 103). The greater differences between predicted and observed concentrations for the other three compounds (di-ethyl phthalate, naphthalene and pyrene) were attirbuted to higher potential for biodegradation than for the seven relatively bio-refractory compounds.

TABLE 103. COMPARISON OF PREDICTED AND MEASURED RETURN ACTIVATED SLUDGE ORGANIC CONTAMINANT CONCENTRATIONS (MELCER AND BRIDLE, 1985)

ORGANICS	RAS CONCENTRATION (mg/kg)		RATIO PREDICTED/ MEASURED
	PREDICTED	MEASURED	
Pesticides/PCBs			
Arochlor 1254	1,249	844	1.48
Heptachlor	295	822	0.36
Lindane	180	27	6.67
Toxaphene	708	259	2.73
Phthalates			
Bis(2-EH) phthalate	462	153	3.02
Diethyl phthalate	649	31	20.93
Dioctyl phthalate	333	91	3.68
PAHs			
Benzo(a)anthracene	280	33	8.48
Naphthalene	1,121	2.9	386
Pyrene	440	16	27.5

In summary, the procedure for modelling the biosorption mechanism is relatively straightforward. A bioconcentration or solids partitioning constant is estimated from the octanol/water partition coefficient, and then the concentration in the solids can be calculated from the effluent (equilibrium) contaminant concentration. The uncertainties of the methodology lie mainly with the biomass used. Blackburn *et al* (1985) used lyophilized sludge to test the adsorptive capacity of the sludge biomass. While they indicate that this inactivated sludge had similar flocculating and settling properties as fresh viable sludge, there was no assurance that the adsorptive properties were not altered. Moos *et al* (1983) and Jones (1984) both used viable activated sludge. The former group were particularly concerned that inactivation was so severe a shock to the biomass that the adsorptive properties would in fact be altered. Use of viable biomass for adsorptive studies may be acceptable if the contaminants are mostly refractory (e.g. Lindane). If compounds that are biodegradable are tested for adsorption with viable biomass, however, it is difficult to differentiate the removal due to biodegradation from that due to adsorption if only mass balance techniques are used.

4.4.2.3 Biodegradation

Organic contaminants may be broken down by activated sludge microorganisms to metabolic products, or ultimately to carbon dioxide. The carbon contained in the organic contaminant may also be incorporated into a cell by synthesis. Again, it is important to distinguish between removal by biodegradation and removal by adsorption or volatilization. Use of radioactive labelled organic compounds is one of the most reliable methods for determining biodegradation, although care must be taken to distinguish radioactive CO_2 from volatilized radio-labelled compound, or radioactivity incorporated into cell mass from adsorbed initial compound.

In the predictive fate study by Blackburn *et al* (1985), compounds with ^{14}C labels were used to determine the biodegradation rates. In the activated sludge reactors, a first order mineralization rate was assumed (although this assumption may be questionable), resulting in the following rate expression:

$$R_{BM} = f_m \cdot C_{ao}/HRT \qquad (23)$$

where:

R_{BM} = Biological mineralization rate, mg/Lhr

C_{ao} = Concentration of ^{14}C-labelled compound at initiation of test, mg/L

f_m = Fraction of feed ^{14}C converted to $^{14}CO_2$

HRT = Hydraulic retention time, hr

The mineralization rate constant was determined to be:

$$K_1^{bm} = \frac{[1/(1-f_m)] - 1}{HRT} \qquad (24)$$

where:

K_1^{bm} = Rate constant, hr^{-1}

Tests were conducted by Blackburn *et al* (1985) in both batch and continuous activated sludge units using phenol, toluene and aniline. Significant discrepancies between mineralization rates for phenol and toluene in the batch and continuous reactors were observed. As a result, it was suggested that batch assays may be inappropriate for estimation of the kinetics of disappearance of a contaminant in a continuous system (Blackburn et al, 1985).

Of the radiolabelled carbon in toluene, phenol and aniline fed to the activated sludge reactors, approximately 26 to 29 percent was converted to cell mass, based on the combined ^{14}C in waste solids plus solids under aeration, divided by the initial ^{14}C level. The net growth of biomass due to utilization of the labelled contaminant was predicted by the equation:

$$DX = \frac{DF \cdot (PC/100)}{f_c} \qquad (25)$$

where:

DX = Net growth of biomass, mg MLSS/day

DF = Conversion of test compound, mg/day

PC = Percent conversion of contaminant carbon to cell carbon

f_c = Weight fraction of carbon in MLSS

Typically the value of f_c is 0.5, and in this study for toluene and aniline, a value of 0.45 was obtained (Blackburn et al, 1985). Calculated cell yields from contaminant biodegradation were estimated for the three test compounds. Predicted yields for phenol and aniline agreed reasonably well with observed daily cell yields, but the observed yield for toluene was considerably higher than the predicted level.

Jones (1984) developed an equation for the biodegradation of non-volatile, non-sorbable organic contaminants. Starting with a mass balance equation of

$$Q_iC_i = Q_eC_e + VK_bC_e \qquad (26)$$

where:

Q_i, Q_e = Influent and effluent flowrate

C_i, C_e = Influent and effluent contaminant concentrations

K_b = Biodegradation rate constant

the rate constant could be estimated by rearranging equation to read

$$K_b = \frac{[C_i/C_e - 1]}{\bar{t}} \qquad (27)$$

where:

$\bar{t}$ = Mean hydraulic residence time

Values of K_b were estimated from batch biodegradation tests using unaerated activated sludge. Volatilization of contaminants and sorption to the reactor walls were shown to be negligible by testing the compounds in control reactors with water only. The effect of biomass sorption was evaluated by inactivating the mixed liquor with mercuric chloride. No change in aqueous concentration was observed over 30 minutes, and removal by biosorption was ruled out. The biodegradation rates were found to be first order; correlation coefficients from linear regression analysis ranged from 0.978 to 0.995. The biodegradation rate constants from the unaerated batch studies are presented in Table 104, together with the predicted removals based on the batch studies, and measured removals in the complete mix flow reactors. The calculated rate constants ranged from 0.58 min^{-1} for benzene to 0.08 min^{-1} for nitrobenzene. Good agreement between measured and predicted removals of the contaminant was achieved.

TABLE 104. BIODEGRADATION RATE CONSTANTS MEASURED IN BATCH DEGRADATION STUDIES, AND COMPARISON OF REMOVALS MEASURED IN CONTINUOUS FLOW BIOREACTORS AND PREDICTED FROM BATCH DEGRADATION STUDIES (JONES, 1984)

COMPOUND	BIODEGRADATION RATE CONSTANT, K_b (min^{-1})	OVERALL REMOVALS (%)	
		MEASURED	PREDICTED
Benzene	0.22	77	74
	0.27	83	77
	0.58	89	88
	0.57	89	88
Toluene	0.15	76	65
	0.27	75	77
	0.16	59	67
	0.33	82	80
Chlorobenzene	0.22	87	81
Ethyl benzene	0.36	82	80
Nitrobenzene	0.08	98	96

Biodegradation studies were also conducted by Jones (1984) with batch aerated reactors containing biomass acclimated to the contaminants. In this set of experiments both volatilization and biodegradation were considered potential removal mechanisms. The overall removal rate expression was given by:

$$-\frac{dC}{dt} = k_o t \qquad (28)$$

where:

k_o = Overall removal rate constant
$= K_b + k_v$

Because it was previously established by Jones (1984), as discussed in Section 4.4.2.1 (Equation 15), that the volatilization rate constant can be expressed as

$$k_v = k_{v,o} + LQ_A$$

Then the biodegradation rate constant is expressed as

$$K_b = k_o - (LQ_A + k_{v,o}) \qquad (29)$$

Experimental data provided estimates of these rate constants, which could then be compared to the predicted values. The results of this set of tests are summarized in Table 105. In all cases, biodegradation was more important than volatilization for removal of benzene, toluene, chlorobenzene and nitrobenzene. The predicted overall removals again agreed well with measured removals.

TABLE 105. RATE CONSTANT AND REMOVAL EFFICIENCIES IN BATCH AERATED BIODEGRADATION RATE STUDIES (JONES, 1984)

COMPOUND	OVERALL RATE CONSTANT k_o (min^{-1})	AERATION RATE Q_a (L/min)	VOLATILIZ. RATE CONSTANT k_{v1} (min^{-1})	BIODEGR. RATE CONSTANT K_{B1} (min^{-1})	OVERALL REMOVAL (%)	
					MEASURED	PREDICTED
Benzene	0.179	4.2	0.078	0.10	65	55
	0.436	4.0	0.074	0.36	75	82
	0.471	4.1	0.076	0.39	81	84
	0.582	4.5	0.084	0.50	88	87
Toluene	0.434	4.2	0.081	0.35	84	81
Chlorobenzene	0.333	4.3	0.053	0.28	87	86
	0.484	4.3	0.053	0.431	84	90
Nitrobenzene	0.09	4.2	<0.001	0.09	98	96
	0.08	4.0	<0.001	0.08	99	96

The removal of phenol from activated sludge by biodegradation using a kinetic approach has been examined (Rozich et al, 1983). The Haldane equation, which is a variation of the Monod expression for cell growth incorporating an inhibition term, was considered the most suitable expression for the experimental results.

Rozich et al (1983) used the Haldane expression and biokinetic constants (e.g. u, Y, K_s) determined from the steady-state pilot plant data using reciprocal plot techniques. Predicted levels of COD and biomass were compared to measured concentrations and biomass production. The results of this model testing evaluation are reported in Table 106. For the most part, agreement between predicted and observed data was good. The model consistently predicted higher levels of phenol than were observed.

Although this model appears to provide a reasonably good estimate of the removal of efficiency of an inhibitory compound such as phenol, the fate of phenol in terms of removal mechanisms is not considered. If the concentrations of phenol in the waste sludge or aeration gases are to be estimated, a different model must be used.

The model developed by Blackburn et al (1985) differentiated between the proportion of the contaminant oxidized to carbon dioxide and the proportion used for cell synthesis in biodegradation. Jones (1984) on the other hand established an overall biodegradation rate, but, before this can be calculated in aerated systems, a volatilization rate constant must be determined assuming negligible biosorption. The procedure of Blackburn et al (1985) requires the measurement of ^{14}C levels in CO_2 off gases and in the initial compound.

4.4.2.4 Overall Removal Mechanism

In a full-scale activated sludge unit, stripping, biodegradation and biosorption may all contribute to the removal of organic contaminants, and hence, any removal expression model should incorporate these mechanisms. The mass balance equation derived by Blackburn et al (1985) for an activated sludge plant was:

TABLE 106. COMPARISON OF VALUES OBSERVED AND PREDICTED BY HALDANE EQUATION (ROZICH ET AL, 1983)

STEADY-STATE RUN NO.	BIOMASS, X (mg/L^{-1})			EXCESS SLUDGE, X (mg/day^{-1})			EFFLUENT SUBSTRATE, S_e (mg/L^{-1})		
	OBSERVED	PREDICTED		OBSERVED	PREDICTED		OBSERVED	PREDICTED	
		COD	PHENOL		COD	PHENOL		COD	PHENOL
1	1745	1791	1777	2794	3367	3192	65(33)	50	19
2	2046	1850	1842	558	1227	1164	58(26)	25	10
3	1606	1561	1551	1132	1536	1457	43(11)	30	12
4	1749	1680	1671	1458	1410	1339	32 (0)	28	11
5	1300	1276	1264	2058	1832	1737	57(25)	39	15
6	1705	1651	1642	1676	1459	1388	36 (4)	28	11
7	1225	1191	1183	955	877	835	54(22)	25	10

* Observed phenol S_e values were never greater than 1 mg/L^{-1}. Numbers in parentheses are observed COD values corrected for the baseline residual COD, 32 mg/L^{-1}.

$$-V\frac{(dC_{ae}^{tot})}{dt} = Q_aC_{ao} - [Q_a-Q_w]C_{ae} - Q_wC_{ae} - [Q_a-Q_w]X_eC_s - Q_wX_rC_s$$
$$- Q_{air}\,C_{air} - V\frac{(dC^b{}_{ae})}{dt} \quad (30)$$

where:

V = Aeration basin volume (L)

$\frac{dC_{ae}^{tot}}{dt}$ = Total net rate of change of soluble substrate concentration in aeration basin (mg/L-day)

Q_a = Influent flow (L/d)

Q_w = Waste sludge flow (L/d)

Q_{air} = Air flowrate (L/d)

C_{ao} = Soluble substrate concentration in influent (mg/L)

C_{ae} = Soluble substrate concentration in effluent (mg/L)

$\frac{(dC^b{}_{ae})}{dt}$ = Net rate of change of soluble concentration of substrate in aeration basin due to biodegradation (mg/L^{-d})

C_s = Substrate loading on biological solids (g/g)

C_{air} = Substrate concentration in exhaust air (mg/L)

X_e = Concentration of biological solids in effluent

X_r = Concentration of biological solids in recycle sludge stream (mg/L)

An equation describing C_{ae}, the effluent soluble substrate concentration was derived by making several substitutions.

The overall mass balance equation at steady-state can be expressed:

$$C_{ae} = Q_aC_{ao}/[Q_a + \frac{XVK_{ow}f_L}{1000\ P_L\ \theta_c} + VK_a^{st}a + VK'\ X] \quad (31)$$

where:

K' = Monod substrate utilization rate contstant (L/mg·min)

From this equation, fractional removals attributable to the mechanisms can be calculated. By setting

$$A = HRT(x)(k_{ow})f_L/1000\ P_L\ \theta_c \text{ (adsorption term)} \quad (32)$$

$$S = HRT(Q_{air}/V)\ 6.18 \times 10^{-5}\ H_c{}^{1.045} \text{ (stripping term)} \quad (33)$$

$$B = HRT\ (K')(x) \quad (34)$$

then Fraction Adsorbed = $A/(1 + A + S + B)$ (35)

Fraction Stripped = $S/(1 + A + S + B)$ (36)

Fraction Biodegraded = $B/(1+ A + S + B)$ (37)

These derivations are all based on the following assumptions (Blackburn et al, 1985):

1. Complete mixing is achieved in the aeration tank.
2. Soluble influent substrate concentration remains constant.
3. All substrate in the influent is in the soluble form.
4. No microbial solids are contained in the raw wastewater to the aeration tank.
5. No bio-oxidation, stripping or sorption occurs in the secondary clarifier.
6. No sludge accumulates in the secondary clarifier.
7. Steady-state conditions prevail throughout the system.
8. No saturation effect is present regarding biomass sorption.
9. Substrate utilization is described by the Monod expression.

Jones (1984) also developed an overall mass balance for the removal of trace contaminants in wastewater treatment plants. The expression developed was:

$$V\left(\frac{dC}{dt}\right) = Q_iC_i - Q_eC_e - V\left(\frac{dC}{dt}\right)_v - V\left(\frac{dC}{dt}\right)_s - V\left(\frac{dC}{dt}\right)_d \quad (38)$$

where:

V = Reactor volume

Q_i, Q_e = Influent and effluent flowrates

C_i, C_e = Influent and effluent substrate concentrations

$\left(\frac{dC}{dt}\right)$ = Rate of change of substrate concentration

$\left(\frac{dC}{dt}\right)_v$ = Substrate removal rate due to volatilization

$\left(\frac{dC}{dt}\right)_s$ = Substrate removal rate due to biosorption

$\left(\frac{dC}{dt}\right)_d$ = Substrate removal rate due to biodegradation

At a steady-state, Equation (38) can be expressed as:

$$Q_eC_i = Q_eC_e + Vk_vC + Vk_bC + qM_sQ_s \quad (39)$$

where:

q = Sorbed mass of substrate per unit biomass

M_s = Mixed liquor suspended solids

Q_s = Sludge wasting rate

Equation (39) is given the acronym STORM (Steady-state Trace Organics Removal Model) by Jones (1984). The author discussed only two particular cases of this model, however, which centred on non-biodegradable organics (i.e. $k_b = 0$), or non-sorbable organics ($q = o$).

For non-biodegradable organics the effluent concentration was expressed as

$$C_e = C_i\,[1\ \bar{t}\cdot k_v + (\bar{t}\cdot M_s\cdot k_B\cdot 10^{-6}/\theta_s\cdot 24)]^{-1} \quad (40)$$

where:

θ_s = Solids retention time

$\bar{t}$ = Mean hydraulic retention time and using a simple relationship established by Mackay (1982) for bioconcentration factor k_B and octanol/water partition coefficient (Equation 22), i.e.

$$k_B = 0.048\ K_{ow}$$

the effluent concentration can be re-defined as

$$C_e = C_i\ [1 + \bar{t}k_v + (\bar{t} \cdot M_s \cdot K_{ow} \cdot 10^{-8.7})/\theta_s]^{-1} \quad (41)$$

From this equation, Jones (1984) observed that as volatility of the contaminant increases, biosorption as a removal mechanism is decreased in importance.

For non-sorbable compounds, the concentration of a contaminant in the effluent can be expressed as

$$C_e = C_i/[1 + \bar{t}(k_v + k_B)] \quad (42)$$

while the contaminant concentration in the off-gas is given as

$$C_g = (Vk_v\ C_e)/Q_g \quad (43)$$

where:

Q_g = Air flowrate

Examination of these expressions leads to the conclusion that as the biodegradation rate constant k_B is increased, the concentration of a contaminant in the off-gas declines.

For compounds in which biosorption played an insignificant role, Jones (1984) was able to evaluate contaminant removal due to biodegradation and volatilization in steady-state laboratory activated sludge units. Among the more interesting results observed in this study were:

i) The biodegradation rate constant did not vary significantly with the system SRT or HRT.

ii) For any specified overall contaminant removal efficiency, as the volatilization rate constant increases, the biodegradation rate constant also increases.

iii) An increase in aeration rate increased both the biodegradation rate constant and the volatilization rate constant.

4.5 Summary of Trace Contaminant Removal Data and Mechanisms

There is a substantial body of data available concerning trace contaminant removals in full-scale activated sludge treatment works. Among other processes, removal efficiencies in the primary clarification process are best characterized. Contaminant removal in that process may be accomplished by sedimentation (e.g. PCBs or pesticides) or by volatilization (chloroform, trichloroethylene). Data on removal efficiencies in other wastewater treatment processes is generally scarce.

In activated sludge plants, metals such as copper, chromium and zinc generally have high removal efficiencies (e.g. 70 percent or higher), while cadmium and nickel have lower removals (e.g. less than 50 percent). Lead and cyanide removals

Metals which are largely insoluble (e.g. lead, chromium and zinc) tend to precipitate and are removed during primary clarification, whereas metals that are soluble (e.g. cadmium, copper, nickel) tend to be either adsorbed by mixed liquor or pass through the system. Soluble metals may be either free or complexed; free metal species may adsorb to the biomass, while complexed metals tend to pass through.

Many researchers consider that pH is the most important factor governing metal removal in wastewater treatment plants. pH levels of 8.0 or higher appear to provide the greatest removal capability. There is general concensus that metals are bound to activated sludge by exocellular polymers in the biomass. The polymers contain many organic functional groups which are pH dependent, and this may explain, in part, the pH dependence of metal removal, other than direct metal hydroxide or carbonate precipitation. Adsorption of metals to the sludge biomass appears to be a physical-chemical process rather than a biological transport process based on tests with live and inactive biomass. Uptake of metals by activated sludge is rapid, with reports that 90 percent of metals being taken up by the biomass in as little as 10 minutes. Adsorption appears to be a more important mechanism than precipitation for removal of metals from settled wastewater.

There is no concensus that SRT control can be used to regulate removal or uptake of metals by activated sludge, especially in full-scale systems.

Removal of organic contaminants is accomplished by either volatilization, biodegradation or biosorption. For most organics, volatilization and/or biodegradation are the principal mechanisms. Biosorption appears to be of limited importance except for compounds such as phthalates and possibly PAHs. For purgeable organics, volatilization may be the most important removal mechanism if the activated sludge is non-acclimated. Conversely, if the mixed liquor is acclimated to the contaminant, biodegradation may be the most important mechanism.

Estimates of the relative importance of the removal mechanisms are generally consistent, but the importance attached to different mechanisms varied considerably for some compounds such as 1,2-dichloroethane and 1,2-dichlorobenzene. Estimates of the contribution of the individual mechanisms for removal of phenols, PAHs and pesticides are generally lacking.

Several attempts have been made to mathematically model the removal mechanisms of trace contaminants in activated sludge systems. Of these models, the volatilization and biosorption models are better developed than the biodegradation model. The predictive equations are derived from steady-state equilibrium conditions, and as such do not represent the typical operation of a real wastewater treatment plant, which is subject to cyclical variation as well as slug inputs. The existing models are not equipped to handle this dynamic behaviour. There has been no field testing of the mathematical models, both because of the inability to describe dynamic fluctuations, and because the biodegradability removal model has not yet been adequately defined. At the present, the models are probably useful indicators of the fate of contaminants in activated sludge plants, but should not be viewed as providing unquestionable results.

The models reviewed to date are concerned with activated sludge systems, and principally diffused aeration processes. Other secondary processes such as rotating biological contactors or trickling filters have not been addressed, nor have other wastewater processes which may effect the behaviour of wastewater contaminants (e.g. sludge processing).

5.0 VARIABILITY OF TRACE CONTAMINANTS AND DYNAMIC RESPONSE OF WASTEWATER TREATMENT SYSTEMS

5.1 Variability of Trace Contaminants

Metal concentrations in raw wastewater, primary effluent, mixed liquor and final effluent were measured at hourly intervals for a three-day period at a Southern Ontario WPCP (Oliver and Cosgrove, 1974). Concentrations for zinc, lead, iron, nickel, copper and chromium in the raw wastewater are depicted in Figure 6. Slug concentrations of zinc, chromium, nickel and copper were observed in the raw wastewater. Hourly samples of raw wastewater were collected over a period of 7 days at the Edmonton, AB Gold Bar wastewater treatment plant (Neilsen and Hrudey, 1983). The hourly fluctuations of the flow and metals are depicted in Figure 1 which is found in Section 3.1. The diurnal flow pattern was consistent through this study. Chromium and zinc were the metals with the most observable spike concentrations. Copper levels were subject to less variation in the raw wastewater. Unfortunately, the sampling frequency was not repeated with the treatment plant effluent, and so influent and effluent concentration relationships could not be established.

Some estimate of the effect of biological treatment on contaminant variability can be made from the Metro Toronto trace organic data. As shown in Table 107, variability of purgeable compounds, as expressed by relative standard deviation of the mean concentration, was high in the influents, frequently greater than 100 percent of the mean value. The range of RSDs for purgeables was 12 to 200 percent of the mean. Similar values were recorded for acid and base/neutral extractable compounds. Pesticide data are limited, but high RSD values were noted for the few compounds observed at detectable concentrations. The high RSD values may partly result from the limited number of grab samples evaluated.

RSD values for the corresponding effluent contaminants are also summarized in Table 107. Although there are fewer compounds detected after biological treatment, the variability of the contaminants in the effluent is generally as great, relative to the mean values, as in the influents. Absolute values of standard deviations were generally less for effluent contaminant concentrations than influent concentrations.

The variability of inorganic contaminants in three Niagara (Ontario) region treatment plant influents and effluents are summarized in Table 108. In most cases, the relative variability about the mean concentration was greater in the effluents than in the influents.

TABLE 108. COMPARISON OF RELATIVE STANDARD DEVIATIONS OF INORGANIC CONTAMINANTS IN NIAGARA REGION WPCP INFLUENTS AND EFFLUENTS

INORGANIC	RELATIVE STANDARD DEVIATION (% of Mean Concentration)					
	WELLAND		FORT ERIE		NIAGARA FALLS	
	INFLUENT	EFFLUENT	INFLUENT	EFFLUENT	INFLUENT	EFFLUENT
Silver	140	-	-	-	-	-
Arsenic	140	230	200	-	200	-
Cadmium (ug/L)	-	330	120	190	200	240
Chromium	77	150	120	130	120	240
Copper	57	170	86	110	28	39
Mercury (ug/L)	160	220	26	47	25	34
Nickel	260	170	200	170	200	240
Lead	110	170	140	190	200	160
Zinc	64	150	31	110	6.1	67
Cyanide	120	200	200	130	190	165

TABLE 107. COMPARISON OF RELATIVE STANDARD DEVIATIONS OF ORGANIC COMPOUNDS IN METRO TORONTO WPCP INFLUENTS AND EFFLUENTS

PURGEABLE COMPOUNDS	RELATIVE STANDARD DEVIATION (% OF MEAN CONCENTRATION)							
	TORONTO MAIN		NORTH TORONTO		HIGHLAND CREEK		HUMBER	
	INFLUENT	EFFLUENT	INFLUENT	EFFLUENT	INFLUENT	EFFLUENT	INFLUENT	EFFLUENT
1,1-Dichloroethylene	63	--	--	--	46.4	200	70	--
Dichloromethane	47.3	48	44	35	38.1	23.1	25.8	33.2
1,1-Dichloroethane	200	--	--	--	150	75.6	130	--
Chloroform	110	72	61	66	15	29	43	39
1,1,1-Trichloroethane	69	--	--	--	41.1	49	45.7	43
Benzene	--	--	200	--	--	--	200	--
Bromodichloromethane	--	--	--	200	--	--	--	--
Trichloroethylene	96	--	--	--	120	200	12	--
Toluene	25.6	130	71	--	167	100	130	170
Tetrachloroethylene	31	200	--	200	70	116	45	--
Ethyl benzene	29.9	200	110	--	110	--	87	120
P- and M-Xylene	24.6	70	15	--	101	200	79.1	81
O-Xylene	32.3	96	35	--	104	--	85.0	79
1,4-Dichlorobenzene(1)	17	11	70	--	43	100	20	13
1,2-Dichlorobenzene(1)	40	38	200	--	200	--	77	80
Phenol	72.6	200	75	200	147	120	114	120
2,4-Dimethylphenol	180	78	41	0	140	36	--	29
p-Chloro-m-cresol	120	--	160	--	--	--	68.4	--
2,4-Dichlorophenol	67	--	70	--	70	--	200	--
Pentachlorophenol	120	67	87	70	200	70	--	67
o-cresol	65.3	--	120	--	130	--	140	120
m-cresol	68.9	--	170	--	120	--	125	120
p-cresol	64.3	--	84.9	--	124	--	107	--
2,4,6-Trichlorophenol	--	--	200	--	200	--	--	--
1,4-Dichlorobenzene(2)	50.9	63	61	34	14.4	49	48	17
1,2-Dichlorobenzene(2)	89.3	63	46	150	100	110	100	31
Naphthalene	76	90	79	--	82	--	110	70
Acenaphthene	--	--	200	--	--	--	0	--
Acenaphthylene	--	--	200	--	--	--	0	--
Diethyl phthalate	36.5	100	42	55	41.6	120	37	120
9H Fluorene	140	--	70	200	70	--	0	--
Phenanthrene	45.2	--	50	--	100	200	0	--
Anthracene	100	0	--	110	200	0	0	90
Di-n-butyl phthalate	50.6	26	100	34	149	30	78.4	39
Fluoranthene	90	--	--	--	160	120	70	200
Pyrene	52	200	120	--	94	70	70	200
Chrysene	120	--	--	--	200	120	0	--
Benzo(a)anthracene	100	--	--	--	100	120	0	--
Bis(2-ethylhexyl) phthalate	43.4	133	104	65	52.8	28.7	22.4	79.6
Benzo(k)fluoranthene	150	ND	--	--	200	120	0	--
Benzo(b)fluoranthene	70	--	--	--	200	--	0	--
Benzo(a)pyrene	--	--	--	--	200	200	0	--
Hexachlorobenzene	--	200	--	--	200	200	--	120
alpha-BHC	--	--	200	200	--	--	--	--
beta-BHC	--	--	200	--	--	--	--	--
gamma-BHC	100	120	164	80	180	100	200	120
4,4'-DDD	--	--	200	200	--	--	--	--
4,4'-DDE	--	200	200	200	--	--	--	--
Dieldrin	--	200	--	--	--	--	--	--
alpha-Endosulfan	--	--	--	200	--	--	--	--
Oxychlordane	--	--	200	200	--	--	--	--
gamma-Chlordane	120	--	--	--	--	--	--	--
Mirex	200	--	--	--	--	--	--	--
Atrazine	--	200	--	--	--	--	--	200
2,4-D	200	--	120	--	200	--	--	--

(1) Measured as purgeable compound.

(2) Measured as extractable compound.

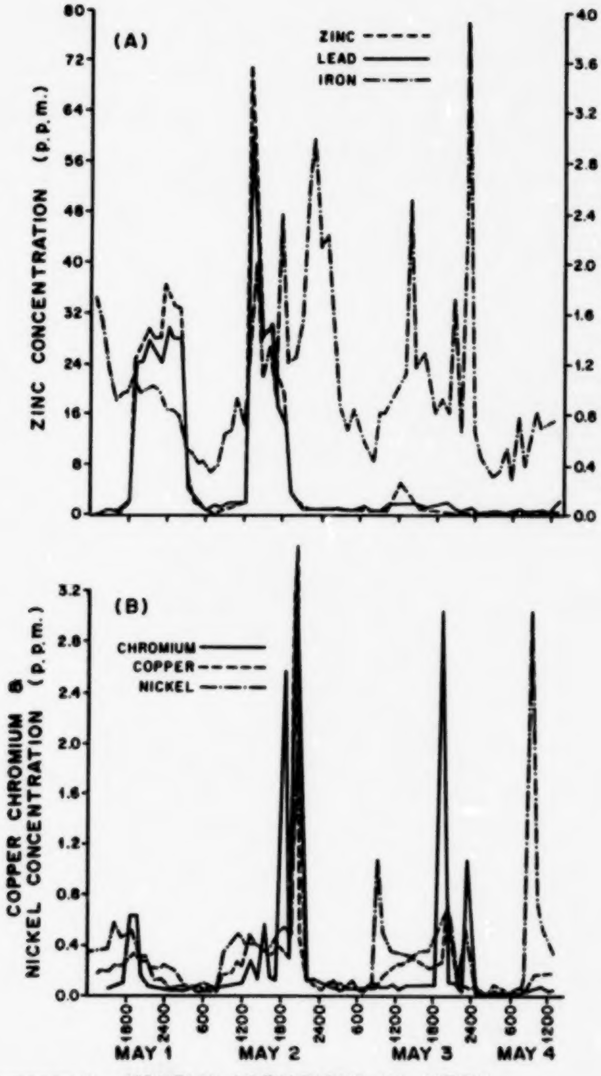

FIGURE 6 — HOURLY VARIATIONS IN METAL CONCENTRATIONS IN AN ONTARIO TREATMENT PLANT INFLUENT (Oliver and Cosgrove, 1974)

VARIABILITY OF TRACE CONTAMINANTS AND DYNAMIC RESPONSE

Estimates of contaminant variability (indicated by relative standard deviation of mean contaminant concentrations) from the 30 day study in Chattanooga, TN are shown in Table 109 (EPA, 1982b). In most cases, the RSD values are greater in the effluent than in the influents. If mean RSD values are calculated for groups of contaminants (i.e. volatiles, base/neutrals, etc.), then there is more variability in the effluent contaminant groups than in the influent groups, with the exception of the inorganics. Even in the conventional contaminants group, the effluent BOD_5 and TSS data were more variable in terms of RSD than the influent concentrations. From this study, then, it appears that a treatment plant does not reduce contaminant variability relative to mean concentrations. Because contaminant levels in the raw wastewater are reduced by approximately an order of magnitude, the standard deviation of mean concentrations in the effluent are about 10 percent of the magnitude of standard deviations of mean levels in influents.

TABLE 109. EFFECT OF BIOLOGICAL TREATMENT ON CONTAMINANT VARIABILITY (FROM EPA, 1982b)

PARAMETER[1]	INFLUENT		EFFLUENT	
	MEAN (ug/L)	RELATIVE STANDARD DEVIATION (%)	MEAN (ug/L)	RELATIVE STANDARD DEVIATION (%)
Volatiles				
Benzene	18	67	4.1	83
1,1,1-Trichloroethane	20	245	5.1	290
Chloroform	73	49	38.	36
Ethyl benzene[2]	23	78	4.4	130
Methylene chloride[2]	88	98	83.	180
Toluene[2]	321	101	55.	220
Trichloroethylene	26	196	4.2	250
Tetrachloroethylene	52	167	7.1	130
Acids				
Phenol	201	77	40.	250
2,4-Dichlorophenol	5	120	2.8	150
Base/Neutrals				
1,2,4-Trichlorobenzene	17	129	6.5	160
1,3-Dichlorobenzene	2	300	1.7	150
1,4-Dichlorobenzene	5	160	0.9	290
Naphthalene	11	100	0.7	420
Bis(2-Ethylhexyl) phthalate	12	120	9.9	400
Di-n-Butyl phthalate	5	280	1.8	220
Diethyl phthalate	4	200	5.4	170
Inorganics				
Chromium	225	234	53.	150
Copper	77	52	26.	110
Cyanide	83	101	88.	130
Mercury (ng/L)	303	89	<300.	-
Nickel	73	104	64.	39
Silver	5	40	1.2	63
Zinc	332	49	100.	46
Conventional				
BOD_5	303	40	36.	53
TSS	232	40	34.	62

1. Influent variability analysis conducted on priority toxic pollutants detected 50 percent of the time or greater for combined 36-day period.
2. Outlier values were removed from database (influent only).

VARIABILITY OF TRACE CONTAMINANTS AND DYNAMIC RESPONSE

Of particular interest in this study is the variability of the influent constituent concentrations. The relative standard deviation (RSD) of each contaminant was calculated for both the 30-d and 6-d studies (Table 110). In the 30-d study, the RSD of the mean ranged from 32% to 300% with copper showing the least variable concentrations, and 1,3-dichlorobenzene showing the highest variability in concentrations. Contaminants present in low concentrations typically were associated with higher RSD values. In the 6-d study, RSD values ranged between 20% and 245% of the mean values. The lowest RSD was associated with copper as was the case in the 30-d study, but the maximum RSD was observed for mercury in the 6-d study. The RSD values are generally higher for any constituents in the 30-d study than the 6-d study. The implication is that a short-term sampling study with a small number of data points may not adequately characterize the variability of a constituent, particularly if composite samples are collected.

TABLE 110. RELATIVE STANDARD DEVIATIONS OF PRIORITY POLLUTANTS
IN INFLUENT SAMPLES DURING
EPA 30 DAY STUDY (FROM EPA, 1982b)

PARAMETER^1	RELATIVE STANDARD DEVIATION (% of Mean)	
	30-DAY STUDY	6-DAY STUDY
Volatiles		
Benzene	67	57
1,1,1-Trichloroethane	245	114
Chloroform	49	76
Ethylbenzene^2	78	85
Methylene chloride^2	98	75
Toluene^2	101	62
Trichloroethylene	196	120
Tetrachloroethylene	167	64
Acids		
Phenol	77	47
2,4-Dichlorophenol	120	100
Base/Neutrals		
1,2,4-Trichlorobenzene	129	45
1,3-Dichlorobenzene	300	100
1,4-Dichlorobenzene	160	75
Naphthalene	100	82
Bis(2-Ethylhexyl) phthalate	120	50
Di-n-Butyl phthalate	280	50
Diethyl phthalate	200	50
Metals		
Chromium	234	71
Copper	52	20
Cyanide	101	35
Mercury	89	245
Nickel	104	38
Silver	40	33
Zinc	49	27
Conventional		
BOD_5	40	26
TSS	40	29

1. Influent variability analysis conducted on priority toxic pollutants detected 50 percent of the time or greater for combined 36-day period.
2. Outlier values were removed from database.

At the Edmonton, Alberta wastewater treatment plant, the relative variability about mean concentrations was higher for some metals in the effluent than in the influent, but the reverse was true for other metals as summarized in Table 111 (Neilsen, 1982). At a Puerto Rican treatment plant, RSD values for metals and phenol were generally higher in the effluent than in the influent (Roman-Seda, 1984).

TABLE 111. COMPARISON OF RELATIVE STANDARD DEVIATIONS OF TRACE CONTAMINANTS IN TWO BIOLOGICAL TREATMENT PLANTS

CONTAMINANT	RELATIVE STANDARD DEVIATION (% of Mean Value)			
	EDMONTON, ALBERTA (Neilsen, 1982)		PUERTO RICO (Roman-Seda, 1984)	
	INFLUENT	EFFLUENT	INFLUENT	EFFLUENT
Cadmium	52	94	-	
Copper	45	20	26	40
Chromium	160	40	46	80
Nickel	19	180	-	-
Lead	-	-	42	80
Zinc	61	62	50	52
Phenol	-	-	66	61

When contaminant concentrations are expressed as arithmetic means with standard deviations, then it appears that the variability of effluent contaminants relative to mean concentrations is a great as in the influents. Actual standard deviations of mean effluent concentrations are typically lower than the corresponding standard deviations of mean influent levels due to removal of the contaminant through the treatment plant.

With respect to the variability of contaminant removal within a plant, from the data of the 30-d study at Chattanooga (EPA, 1982b), as shown in Table 112, it is clear that removal is not always consistent from day to day. The removal of the conventional pollutants, BOD_5 and TSS, and the purgeable contaminants, benzene, toluene and tetrachloroethylene, were consistent from one day to the next, as indicated by the RSDs of the removal efficiency, with values less than 25 percent. For other contaminants such as methylene chloride, 2,4-dichlorophenol, 1,3-dichlorobenzene, diethyl phthalate, cyanide, mercury and nickel, removal efficiencies were highly variable. The greatest amount of variation in removal efficiency was associated with those contaminants having low mean removal efficiencies.

TABLE 112. EVALUATION OF WITHIN PLANT CONTAMINANT REMOVAL VARIABILITY (FROM EPA, 1982b)

CONTAMINANT	MEAN REMOVAL EFFICIENCY (%)	STANDARD DEVIATION OF MEAN REMOVAL (%)	RELATIVE STANDARD DEVIATION (% of Mean)
Volatiles			
Benzene	77	10	13
1,1,1-Trichloroethane	80	27	34
Chloroform	43	23	52
Ethyl benzene	79	29	37
Methylene chloride	37	30	80
Toluene	87	13	15
Trichloroethylene	83	27	32
Tetrachloroethylene	85	19	22
Acids			
Phenol	86	26	30
2,4-Dichlorophenol	50	42	84
Base/Neutrals			
1,2,4-Trichlorobenzene	62	30	49
1,3-Dichlorobenzene	56	46	83
1,4-Dichlorobenzene	75	35	47
Naphthalene	90	27	31
Bis(2-ethylhexyl) phthalate	65	40	62
Di-n-butyl phthalate	62	46	74
Diethyl phthalate	22	36	170
Inorganics			
Chromium	61	31	50
Copper	69	24	35
Cyanide	21	29	140
Mercury	27	23	83
Nickel	24	22	93
Silver	73	16	46
Zinc	66	20	30
Conventionals			
BOD_5	88	4.9	5.5
TSS	84	11	13

5.2 Dynamic Response of Treatment Plants to Variable Trace Contaminant Concentrations

From the above discussion, it was shown that even conventional pollutants, with a high removal efficiency, are subject to fluctuating influent and effluent concentrations. Data from the 30 day study (EPA, 1982b) indicate that trace contaminant levels in influent and effluent samples are subject to even greater concentration variability based on daily 24 hour composite samples. Estimates of variability based on short-term fluctuations of trace contaminant levels are probably at least as great as in the daily composites, but there are few data to confirm this. A limited database characterizes fluctuating levels of metals in raw wastewater (Oliver and Cosgrove, 1974; Neilsen and Hrudey, 1983) but not effluents. Data on the short-term variations of trace organic concentrations are lacking completely. Consequently, there are no full-scale data on which to assess the dynamic response of treatment plants to fluctuating trace contaminant levels.

VARIABILITY OF TRACE CONTAMINANTS AND DYNAMIC RESPONSE

The dynamic response of activated sludge plants to fluctuating concentrations of conventional pollutants has been investigated. For example, influent and effluent BOD concentrations and flow data from a Wisconsin treatment plant, collected at hourly intervals over a two week period, are presented in Figure 7 (Berthouex _et al_, 1978). Diurnal fluctuations in the flow and raw wastewater BOD concentration were particularly evident. A first order stochastic model describing the dynamic fluctuations accounted for 75 percent of the variability of the effluent data. Although the treatment plant effectively dampened out variations in influent BOD levels, the response of the activated sludge system (i.e. effluent BOD concentration) to the influent BOD level was significant.

BOD and TSS concentrations in the primary effluent and final effluent of the Brantford, Ontario WPCP were monitored at four hour intervals for one week to assess the response of the treatment plant to fluctuating pollutant concentrations (MacGregor, 1975). A lag period of 4 to 8 hours between influent and effluent concentrations was noted. A linear transfer function model provided good forecasting capability for effluent BOD_5 data. The effluent BOD_5 and TSS concentrations were found to be significantly affected by the fluctuating influent concentrations.

Variability of influent concentrations based on TOC measurements was simulated with random, pulse and step function inputs (Novotny _et al_, 1976). For the random inputs, theoretical and observed effluent TOC levels were generally within 5 percent. The observed error for the pulse and step function models was 13 and 2 percent, respectively. It was concluded that the models provided good predictive capability. Complex influent variation patterns can be simulated by superposition of pulse, step and harmonic functions plus a random signal (Novotny _et al_, 1976).

Slight increases in soluble effluent COD were observed in laboratory activated sludge units when square-wave transients of amplitude 2.8 X normal were applied, and significant increases in soluble effluent COD were found during transient loadings of greater than 4 X normal (Selna and Schroeder, 1978). The data indicated that there was no advantage in operating at a 5 d SRT compared to 10 d for soluble COD removal during transient loads.

Only one study was identified which indicated that the effluent COD concentrations in an industrial activated sludge plant could not be related to influent levels using time series analysis (Debelak and Sims, 1981). A time series transfer function model based on influent and effluent BOD or COD data alone was considered to be inadequate to accurately predict the response of activated sludge plants to variable inputs. This may be in part due to sample collection (one grab per day), and partly due to the efficient operation of the treatment plant, which produced a consistent effluent quality in spite of variable COD inputs.

The effect of activated sludge treatment on the concentrations of total and dissolved zinc in primary effluent and final effluent are illustrated in Figure 8 (Oliver and Cosgrove, 1974). Most of the total zinc was removed in the primary clarifiers. The effluent concentrations of total and dissolved zinc did not show the spike dosages which were observed in the raw

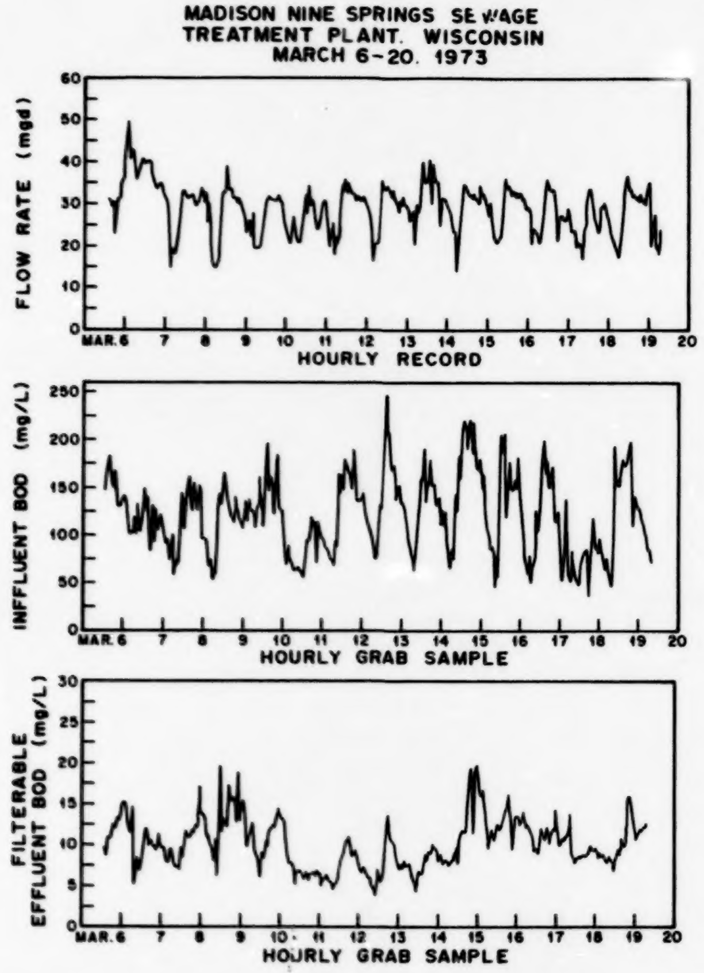

FIGURE 7—INFLUENT AND EFFLUENT HOURLY DATA FOR 14-DAY SURVEY, MARCH 1973 AT MADISON WI POLLUTION CONTROL PLANT (Berthouex *et al*, 1978)

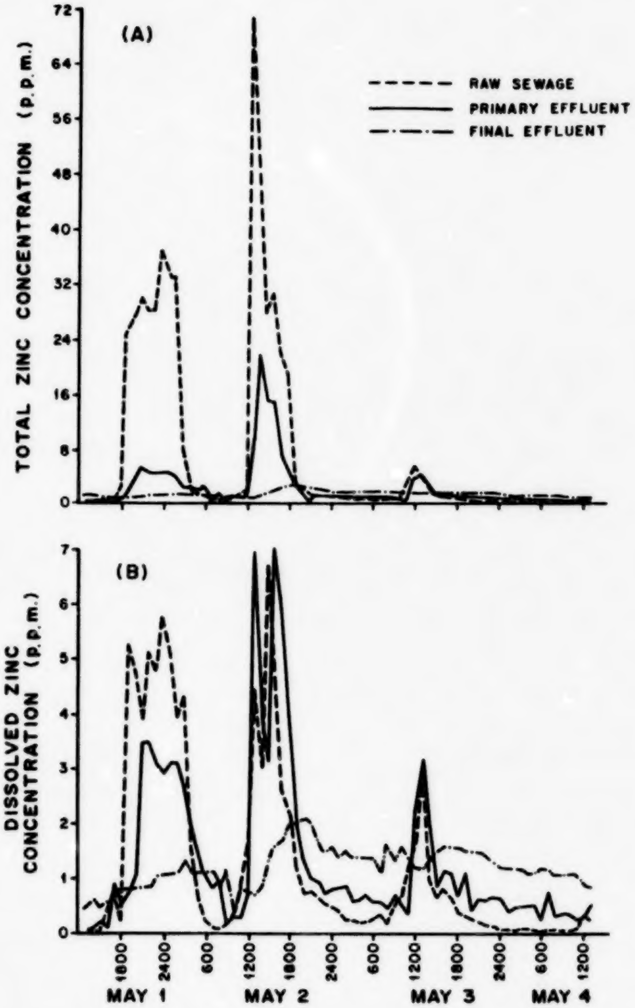

FIGURE 8 — HOURLY CHANGES IN ZINC LEVELS IN THE RAW SEWAGE, PRIMARY EFFLUENT AND SECONDARY EFFLUENT [(A) TOTAL, (B) DISSOLVED] OF AN ONTARIO TREATMENT PLANT (Oliver and Cosgrove, 1974)

wastewater and primary effluent. The final effluent concentrations of both total and dissolved zinc did remain higher than the raw wastewater or primary effluent concentrations after the slug doses subsided (Oliver and Cosgrove, 1974).

A pilot-scale wastewater treatment plant was subjected to shock loadings of metals, resulting in influent levels five to ten times higher than background concentrations (Rossin et al, 1982). The activated sludge pilot plant was able to exert a significant dampening effect on the slug con centrations. The data indicated, however, that for metals such as cadmium and nickel, an increase in the influent metal concentration would result in higher effluent levels (i.e. there was a response to the influent fluctuations). It was concluded that the mixed liquor had limited capacity to adsorb slug dosages of cadmium and nickel (Rossin et al, 1982). Elenbogen et al (1985), conversely, indicated that activated sludge systems were capable of handling transient concentrations of cadmium if the mixed liquor suspended solids/cadmium ratio was greater than 1000. In this case, instantaneous adsorption of soluble cadmium would take place, preventing loss of cadmium in the effluent.

From investigations of the response of a laboratory-scale activated sludge plant to trace contaminants applied as either spike or square wave additions, some of the more pertinent conclusions were (Jones, 1984):

i) Concurrent spiking of benzene, ethyl benzene and chlorobenzene which resulted in influent concentrations of 6000 to 10,000 ug/L for each compound did not affect the activated sludge system performance, while removal efficiencies of these purgeables compounds increased slightly to approximately 90 percent from approximately 85 percent.

ii) Spiking of biodegradable compounds, resulting in an order of magnitude increase in concentration (i.e. from 100 to 1000 ug/L) in the influent, resulted in only small temporary increases in effluent and off-gas concentrations.

iii) Concentrations of biodegradable compounds in effluent and off-gas samples were unaffected by increases in the raw wastewater concentrations over a range of 100 to 2000 ug/L, indicating that biodegradation was more important at the higher concentrations.

iv) In continuous loading studies, interruption of the trace contaminant feed for 2 to 3 days did not affect the biodegradation of benzene, toluene, ethyl benzene, o-xylene, chlorobenzene and nitrobenzene.

v) An interruption of 14 days during simultaneous feeding of benzene, toluene, ethyl benzene, o-xylene and chlorobenzene caused reduced removal due to biodegradation for a period of 2 to 3 days, after which previous steady-state removal efficiencies were resumed.

vi) When benzene, ethyl benzene and chlorobenzene were added to a reactor on the schedule 2 days on and 3 days off, acclimation periods were nearly 3 to 4 times longer, and removals of ethylbenzene and chlorobenzene were less than those observed during continuous addition. Benzene removals during continuous or square wave additions were approximately equal.

vii) Increasing the interval of non-addition of benzene, ethylbenzene and chlorobenzene from 3 days to 6 days had no additional effect on biodegradation.

VARIABILITY OF TRACE CONTAMINANTS AND DYNAMIC RESPONSE

In phenol-acclimated laboratory activated sludge units, increases in the phenol feed concentration from 500,000 to 1,000,000 ug/L were accommodated by the activated sludge system without difficulty (Rozich et al, 1985). An increase of phenol from 1,000,000 to 3,000,000 ug/L resulted in eventual failure of the activated sludge process as evidenced by high effluent levels of phenol and suspended solids, and pronounced changes in the microbial populations of the mixed liquor.

The studies with metals suggest that the activated sludge treatment system will have a dampening effect on spike loadings of these contaminants. In other words, the increase in amplitude of the effluent concentration is expected to be substantially less than amplitude of the contaminant spike in the influent. Concentrations of metals in the effluents do appear to be influenced by the levels in the raw wastewater (Oliver and Cosgrove, 1974; Rossin et al, 1982).

The laboratory-scale work by Jones (1984) indicates that when organic compounds are encountered on an intermittent basis in activated sludge plants, the removal efficiency due to biodegradation is apt to be less than removals in a system receiving the contaminant on a continuous basis. Activated sludge systems receiving constant low concentrations of trace organics are much more capable of removing any slug dosages as a result of increased biodegradation.

6.0 MODELS FOR MANAGEMENT OF TRACE CONTAMINANTS IN SEWER SYSTEMS

The variability of trace contaminant levels in wastewater treatment plant effluents may be reduced by either:

i) management of contaminant concentrations in sewers;
ii) optimum control of the biological wastewater treatment process;
iii) optimum control of internal recycle streams in the wastewater treatment plant.

The impact of activated sludge process control or internal recycle stream management on effluent contaminant variability has not been assessed. Efforts have been made to manage the levels of trace contaminants in sewers through the use of municipal bylaws and development of models predicting contaminant concentrations in sewers.

One of the initial attempts to predict the levels of contaminants in sewers was conducted by A.D. Little, Inc. (1979). In this study, the contributions of residential, commercial and industrial zones to the contaminant load entering wastewater treatment plants in Cincinnati, OH, Hartford, CT, Atlanta, GA, and St. Louis, MO were assessed. For each of the four wastewater drainage basins, certain demographic and economic data were required including:

i) Current population
ii) Land use (residential, commercial, industrial, open)
iii) Number, age and types of residences (single, multiple, apartment)
iv) Characteristics of commercial areas (number of establishments, size)
v) Characteristics of industrial areas (number of industries, size, SIC categories, etc.)

The study investigated 47 residential areas, 12 commercial areas and 21 industrial areas. No industrial zones were identified in the Cincinnati (Muddy Creek) and Hartford sewersheds.

A mass balance approach was used by A.D. Little (1979) to estimate the loadings of contaminants to a water pollution control plant. The expression developed was

$$\mathrm{POTW}_i = \mathrm{RES}_i + \mathrm{COM}_i + \mathrm{IND}_i \qquad (44)$$

where:

POTW_i = Total mass of contaminant i entering POTW (publicly owned treatment works

RES_i = Mass of contaminant i entering POTW from residential sources

COM_i = Mass of contaminant i entering POTW from commercial sources

IND_i = Mass of contaminant i entering POTW from industrial sources

The contribution of RES_i was established by initially establishing a per capita mass contaminant loading:

$$\text{RES.AVG.} = \text{Mass}_i/\text{person}\cdot\text{d} = \frac{(\text{Avg. RES Conc'n i})\,(\text{Total Res. Flow})}{\text{Residential Population}} \qquad (44)$$

from which a total loading could be calculated

RES_i (kg/d) = RES.AVG. (mg/cap.d)(Basin Population)(10^{-6} kg/mg)

For commercial loading of contaminant i, the expression developed was

COM_i (kg/d) = (Avg. COM concentration i)(Commercial Flow)

The industrial loading was expressed by

IND_i (kg/d) = (Avg. IND concentration i)(Industrial Flow)

The contaminant data from residential and commercial sources were relatively consistent in terms of numbers, types and concentrations of contaminants. Thus, it was concluded that use of an average concentration for residential and commercial zones was justifiable. The contaminants and their concentrations found in industrial zones were highly variable, however, and use of an average industrial concentration was not considered valid, especially when the industrial component of the total contaminant load was usually the most significant. Consequently, sampling programs in industrialized areas would be required for estimation of industrial loadings. Use of an average industrial contaminant concentration, without consideration of the number, size or types of industries, was a major weakness of this model.

As a means of "field testing" the mass loading model, the average concentrations derived from the study were used to establish loadings to the four treatment plants investigated in their project. Reasonably good agreement between predicted levels in the treatment plant influent and observed levels were achieved. A more valid test would have involved sampling at other treatment plants independent of the field testing portion of the study.

The A.D. Little (1979) model was a useful indicator of pollutant loadings to wastewater treatment plants. It was valid only for dry weather flow, however, and did not consider the impact of storm events on the wastewater flows or contaminant concentrations. In addition, the impact of infiltration/inflow was not evaluated in this model. A similar but more detailed model for predicting levels of hazardous contaminants in wastewater collection systems is termed the HAZPRED model (Zukovs et al, 1986). Concentrations and loadings of hazardous contaminants in dry weather sewage, and of volumes and loadings of contaminants in urban runoff and combined sewer overflows (CSO) can be predicted by the model. Both separate and combined sewage collection systems can be addressed.

The HAZPRED model for dry weather flow is similar to the mass balance model derived by A.D. Little (1979). There were some modifications to the Little model which help to refine HAZPRED's ability to predict contaminant concentrations in sewers. Rather than assuming a daily per capita use, such as 100 U.S. gal/cap•d as employed by the A.D. Little model, actual water meter readings were used where possible, or failing that, flow data from a water pumping station with an allowance of 10 to 15 percent for water lost in distribution were used.

The Level I HAZPRED model was almost identical to the A.D. Little model, except that a dry weather infiltration/inflow term was incorporated to account for dilution of the collected wastewater. The infiltration term was based on sewer age, sewer network density in the drainage area, and groundwater levels. An allowance of 91 to 227 L/cap·d is typical in Ontario (Zukovs et al, 1986).

The Level II HAZPRED model refined the industrial contaminant contribution by:

i) using industrial wastewater characterization data listed by SIC group in the 1980 edition of the EPA "Treatability Manual";

ii) using the A.D. Little average industrial contaminant concentration data for SIC groups not included in the Treatability Manual;

iii) differentiating between industrial process wastewater, in which the contaminants would be found, and cooling water, which was assumed to contain no contaminants at detectable levels;

iv) assuming a factor of 0.85 as the amount of water returned to the sewer (after losses to steam and product formulation) relative to the amount of water entering the industry.

The dry weather flow in the HAZPRED Level II model is expressed as

$$Q_{TOT} = POP.RWW + CWW + \sum_{k=1}^{m} IPW_k + \sum_{k=1}^{m} ICW_k + DWI \quad (46)$$

where:

Q_{TOT} = Total wastewater flow (L/d)

POP = Catchment basin population

RWW = Residential per capita wastewater flow (L/cap·d)

CWW = Commercial wastewater flow (L/d), including retail stores, offices, institutions such as universities, laundries (car washes, laundromats)

IPW_k = Total industrial process and sanitary wastewater discharged by the industries in the k^{th} SIC group (L/d)

ICW_k = Total cooling water discharged by industries in the k^{th} SIC group to a sanitary or combined sewer (L/d)

DWI = Dry weather infiltration rate (L/d)

The total mass loading rates of specific trace contaminants by the Level II HAZPRED model is given by:

$$M_{TOT_i} = POP.RWW.RC_i + CWW.CC_i + \sum_{k=1}^{m} IPW_k.IC_{i,k} \quad (47)$$

where:

RC_i = Concentration of contaminant i in residential component of wastewater (ug/L)

CC_i = Concentration of contaminant i in commercial component of wastewater (ug/L)

$IC_{i,k}$ = Concentration of contaminant i in wastewater discharged by industries of the k^{th} SIC group (ug/L)

M_{TOT_i} = Total mass rate of contaminant (ug/d)

In this model, it was assumed that industrial cooling water and dry weather infiltration contain no contaminants.

The overall concentration of a trace contaminant i is given by

$$C_i = M_{TOTi}/Q_{TOT} \tag{48}$$

Field testing of the HAZPRED model occurred over a fifteen day period at two catchment areas in Toronto, Ontario. The characteristics of the catchment areas are reported in Table 113. The York catchment basin was dominated by residential land use, while the North York catchment was almost entirely industrial with no residential land use.

TABLE 113. CATCHMENT CHARACTERISTICS FOR HAZPRED MODEL TESTING (CANVIRO CONSULTANTS LTD., 1985)

Catchment	York	North York
Area (ha)	147	354
Sewerage	Combined; pre-1960 installation	Separate; post-1960 installation
Land-Use Distribution		
Residential	55%	0%
Commercial	11%	16%
Industrial	29%	84%
Other	≈ 5%	0%
Number of Industries & Major Commercial Establishments	13	approx. 600
Average Dry Weather Wastewater Flow (L/d)	2,151,000	6,463,000

Predicted wastewater flows were within 20 percent of observed rates in the York catchment, and within 30 percent in the North York Catchment. A comparison of predicted and observed contaminant concentrations is provided in Table 114. In the York catchment, 50 percent of the predicted contaminant concentrations were within 1/2 log of the observed levels, and 82 percent were within 1 log of the observed values. In the North York catchment, 29 percent of the predicted concentrations were within 1/2 log of the observed concentrations and 71 percent were within 1 log of observed levels. The HAZPRED model suffered reduced accuracy in predicting contaminant concentrations in the more industrialized sewer catchment. The reduced accuracy is a result of the incomplete database for industrial wastewater contaminant concentrations, which contribute the greatest loading to the sewers.

TABLE 114. SUMMARY BY CONTAMINANT GROUP OF OBSERVED AND PREDICTED CONCENTRATIONS FROM LEVEL II HAZPRED MODEL (CANVIRO CONSULTANTS LTD., 1985)

LOCATION	CRITERIA	PURGEABLE		EXTRACTABLE ACID		EXTRACTABLE B-N		METALS AND CN^-		TOTAL	
		NO.	%	NO.	%	NO.	%	NO.	%	NO.	%
York	1/2 Log	6	40	0	0	5	63	6	75	17	50
	1 Log	12	80	2	67	7	88	7	88	28	82
North York	1/2 Log	5	26	0	0	3	38	3	38	11	29
	1 Log	15	79	2	67	5	63	5	63	27	71

Notes: 1) Criteria are: Predicted Conc'n within ± 1/2 log (Observed Conc'n) or Predicted Conc'n within ± 1 log (Observed Conc'n)

2) No. = Number of compounds in contaminant class meeting criteria.

3) % = Percent of compounds in contaminant class meeting criteria.

The quantity and contaminant levels of CSO are estimated in the HAZPRED model by simple mass and volume balance relationships based upon the relative proportions of urban runoff and dry weather sewage. Probability density functions derived from the mass and volume balances are then used to describe the distributions of CSO volumes and contaminant loadings. The wet weather models have not yet been verified by field testing.

A computerized program termed SUBAS (Simcoe Engineering Group Ltd., 1984) has been developed to establish sewer-use bylaw contaminant limits based on a number of criteria, including receiving water quality [from the Ontario Ministry of the Environment's "Blue Book" (MOE, 1984)], mixed liquor biomass and anaerobically digested sludge biomass toxicity, contaminant removal efficiency and guidelines for applying digested sludge to agricultural land [MOE/OMAF (Ontario Ministry of Agriculture and Food, 1981)]. Flow considerations and mixing zones in receiving waters are also considered.

The program establishes the worst case concentrations of specific contaminants in raw wastewater that a treatment plant could accept without adversely impacting on process efficiency or on environmental quality. The program then estimates the concentrations in the raw wastewater based on mass loadings from contributing industries. If the calculated concentrations based on industrial loadings exceed the worst case levels, then limits to the contaminant concentrations by industry are required, and the appropriate reduction by industry can be calculated.

The program was tested at two wastewater treatment plants in the Region of Durham, and one treatment plant in the Region of Halton. Some potential problems were identified as a result of field testing. This included negative bylaw limits which were occasionally calculated when the background water concentrations exceeded the MOE Blue Book limit, or when a non-industrial default concentration was greater than the calculated worst quality influent limit. The default database for contaminants in non-industrial wastewater is a listing of literature values, which may or may not be representative of the local conditions. Default values for toxic levels of contaminants to activated sludge biomass, and anaerobic or aerobic sludge microorganisms may also be non-representative. Finally, the model is limited by an adequate database characterizing contaminant levels in industrial wastewaters.

At the present state development, neither the HAZPRED model nor SUBAS program individually can predict both contaminant concentrations in sewers and the maximum concentrations in sewers required to protect either biological wastewater processes or the quality of the waters receiving a treatment plant effluent. In other words, there is no comprehensive management model for controlling trace contaminant levels in sewers. Such a management procedure could be implemented by combining the HAZPRED and SUBAS models. Initially, SUBAS would be used to specify the maximum allowable concentrations of contaminants in the raw wastewater entering a wastewater treatment plant. The HAZPRED model would then be used to predict the concentrations of contaminants in the wastewater arriving at the treatment plant. If the levels of contaminants predicted by HAZPRED exceeded the maximum allowable concentrations stipulated by SUBAS, then industrial contributions would have to be reduced by pretreatment programs. Adjustment of contaminant concentrations discharged by industries in various SIC groups in the HAZPRED model would show the extent to which industrial contaminant discharges would have to be controlled.

Both models at present suffer from an inadequate database characterizing contaminant levels in industrial discharges, as well as an inability to deal with fluctuating contaminant concentrations. The combined SUBAS/HAZPRED model would have to specify an allowable maximum variability in effluent contaminant concentrations to be able to stipulate the maximum raw wastewater variability, provided that the effluent levels were shown to be a response to influent levels.

7.0 ANALYSIS OF TECHNICAL REVIEW

7.1 Summary

In the last six to seven years, the database on trace contaminant concentrations in wastewater streams has expanded significantly due to improved analytical techniques and lower detection limits. In raw municipal wastewater samples, metals, purgeable organics and phthalate esters have been identified as the most frequently occurring compounds. In terms of concentrations, metals are typically found in the range 100 to 1000 ug/L, while the organics may range from 1 to 100 ug/L. Pesticides and PCBs are typically found in the concentration range 0.010 to 1.0 ug/L. Wastewater characteristics can vary considerably from site-to-site in terms of compounds present and their concentrations. The degree of industrialization of a sewer collection area strongly influences the characteristics of the wastewater.

Metal contaminants predominate in treated effluent samples, both in terms of frequency of occurrence and concentration. The types of organic compounds observed in effluents often depends on whether the discharge has been chlorinated. Chlorinated effluents frequently have concentrations of some purgeable organics such as methylene chloride and chloroform which exceed the influent levels. In non-chlorinated effluents, purgeable compounds are usually removed to a high degree (e.g. 90 percent plus) but still may be present at detectable levels. Phthalate esters are among the more commonly occurring organic compounds in effluent samples. Phenolic compounds, with the possible exception of pentachlorophenol, are removed to low levels near the detection limit. Very low levels of pesticides are encountered sporadically.

Industrial discharges are not as well characterized due to the diversity of industries, and the differences within an industrial category due to process age and configuration. Industrial wastewaters generally contain elevated concentrations of some contaminants which are industry-specific. The lack of industrial wastewater characterization data is a major weakness in models for management of sewer use, such as HAZPRED and SUBAS.

Digested sludges have been widely characterized for metal concentrations, due to the concern related to spreading of sludge on agricultural land. Trace organics in sludges have not been as well characterized because the sample matrix has presented problems in the extraction step, leading to high background interferences and high detection limits. Metals are the most frequently occurring contaminants in sludge, and found at the highest levels. Bis(2-ethylhexyl) phthalate, some aromatic solvents (toluene, benzene) and polynuclear aromatic hydrocarbons are also frequently detected in sludge samples.

Process side streams in wastewater treatment plants have been poorly characterized. From the limited data available, some recycle streams in a pollution control plant, such as digester supernatant or heat treatment liquor, have the potential to return high levels of metals and some organics (e.g. purgeables such as benzene or toluene and phenol) to the head of the treatment plant. The data indicate that significant quantities of trace contaminants in these recycle streams may be associated with suspended solids. Other process streams, such as the filtrate from dewatering of sludges, have relatively low or non-detectable levels of contaminants. The relative contribution of the internal streams to the plant loading of trace contaminants or to the effluent trace contaminant concentrations is not well defined by any of the existing plant monitoring data.

Removal of a specific contaminant varies considerably between treatment plants. This variability may relate to plant operation in terms of SRT, aeration rate, and hydraulic loading. In most cases, parameters defining plant operating condition at the time of trace contaminant sampling have been poorly reported. Within a contaminant group such as metals, it is apparent that some contaminants, such as copper, are removed to a greater extent, than others, such as nickel. The same is true for organic contaminants, but the issue is complicated by the potential acclimation of the mixed liquor biomass to the contaminants. Removal efficiency in a wastewater treatment plant appears to be both contaminant-specific and site-specific. Although it may be possible to estimate an approximate removal efficiency, especially for metals, at the present time and with the present knowledge of trace contaminant behaviour, an accurate estimate of removal efficiency requires monitoring at the treatment plant in question.

For metals, the mechanisms contributing to removal are precipitation and adsorption. At low metal concentrations (e.g. less than 1,000 ug/L), adsorption to mixed liquor solids is considered the main removal mechanism. At high metal levels (e.g. greater than 10,000 ug/L), precipitation becomes an important mechanism. The system pH is an important factor governing metal removal, with higher removal efficiencies observed above pH = 8. While much of the particulate metal concentration is reduced by primary clarification, soluble metal levels are lowered by secondary treatment. Complexation of the metal ion with soluble organic ligands may result in the metal passing through the treatment system, and it has been proposed that the concentration of the free metal ion in the aeration basin is the factor governing adsorption by the biomass (Neilsen _et al_, 1984).

The mechanisms contributing to organic contaminant removal in activated sludge systems are volatilization (stripping), biosorption and biodegradation. A database is being developed defining the contributions of the three mechanisms to the overall removals of contaminants observed. This database applies primarily to EPA priority pollutants. In acclimated systems, biodegradation generally is the predominant removal mechanism for all classes of organic compounds. In unacclimated systems, volatilization may be the most important mechanism for removal of purgeable compounds. The contribution of biosorption to removal appears to be significant for contaminants such as phthalates, and although it may be for pesticides and PAHs as well, data are lacking to confirm this. One study (Lurker _et al_, 1982) has suggested that removal of purgeable compounds _at the_ head of the treatment plant (e.g. wet well and aerated grit chamber) may be significant.

Mechanistic models predicting the fate of trace contaminants are being developed. Volatilization appears to be one of the most easily modelled processes because the expressions use Henry's law constant, which is well characterized for many trace organics. Stripping rates in both clean water and samples containing mixed liquor, salts, surfactants and other substances have been evaluated. There is some debate as to whether mixed liquor solids affect the stripping rates of contaminants relative to clean water. Adsorption modelling generally makes use of traditional isotherm techniques, although concentration factors can be calculated predicting sludge concentrations based on treatment plant operating conditions, and raw and final effluent concentrations. The major problem is the potential substrate utilization by the biomass during the adsorption studies. In order to avoid this, authors have variously used freeze-drying (lyophilization), autoclaving and testing at 4°C to inactivate the microorganisms. The question remains as to whether inactivated biomass has identical adsorptive properties as normal biomass. Biodegradation studies typically involve the use of radio-actively labelled compounds, and follow the production of $^{14}C\text{-}CO_2$. Rate equations can be developed, but no mechanistic model can be derived because of the diversity of microorganisms and enzymes involved. The recovery of metabolites carrying the radioactive tag, as well as labelled carbon incorporated into the biomass during synthesis needs to differentiated from the labelled parent compound adsorbed to the biological solids.

Sparse information is available with respect to fluctuations of trace contaminant concentrations in wastewater treatment plant influents and effluents. Through intensive monitoring of influent metal levels, a few studies have indicated that spike concentrations of metals can occur in treatment plant influents. One study (Oliver and Cosgrove, 1974) indicated that these spikes of metals will be attenuated through the treatment plant, but little information is available with regard to the response characteristics of the process to these influent spikes.

A number of studies using time series modelling techniques have concluded that effluent concentrations of conventional pollutants (e.g. BOD, TSS) are correlated to fluctuating influent levels. There are insufficient data for trace contaminants to develop process response relationships at the present time.

Few models have been developed that predict the concentrations of trace contaminants in wastewater collection systems. An initial study by A.D. Little (1979) prepared a mass balance model based on measurement of contaminants in four cities in residential, industrial and commercial areas. This procedure was enlarged by CANVIRO Consultants Ltd. (1985) with their HAZPRED model, which can (i) calculate dry weather flow concentrations and loadings in sewered wastewater, (ii) urban runoff concentrations and loadings, and (iii) combined sewer overflow event contaminant loadings and concentrations.

These models for prediction of trace contaminant concentrations are limited by estimates of trace contaminants in industrial discharges. The only model presently available to predict the maximum allowable influent concentration to a facility, SUBAS, suffers from a lack of removal and biosorption data for many trace contaminants. Both HAZPRED and SUBAS are currently able to predict and manage steady-state trace contaminant concentrations, rather than the dynamic fluctuations observed in actual operation of wastewater treatment systems.

7.2 Data Deficiencies

The vast majority of the municipal STP data reported to date concerns the EPA priority pollutants. Other non-priority pollutant organic compounds are reported in Ontario data, which are relatively limited. These data do indicate the presence of non-priority pollutants including solvents such as xylene, ether and dioxane.

ANALYSIS OF TECHNICAL REVIEW

Data are not consistently presented in all the studies, creating difficulties in comparing the results. Results may be variously reported as arithmetic means, medians or geometric means. The method of reporting may be a function of the data collected. Sludges may be reported on a wet weight or dry weight basis with no indication of the corresponding solids concentrations. When data are evaluated, non-detectable levels may be ignored (i.e. only detectable levels are included for averaging), considered as zero values, or set at the method detection limit. Detection limits have been dropping steadily since trace contaminant concentrations were initially reported a decade ago. Consequently, older studies tend to have more non-detectable levels for organic contaminants (i.e. none less than 10 ug/L for example) while more recent studies have lower detection limits, and more reported concentrations. Evaluation of removal efficiencies is complicated when the concentrations are close to the detection limit.

Sampling frequency is typically inconsistent when several sources of data are reviewed. Results may be reported based on one annual sample, 12 monthly samples, or a series of mean monthly concentrations. The results may be based on a single grab sample or a flow-proportional 24 hr composite sample. It is pointless to try to estimate contaminant variability for example, by averaging monthly mean values, wherein the fluctuations have been averaged out.

A comparison of results from lab-scale or pilot-scale activated sludge units is complicated by the use of different methodologies. Specific concerns related to methodology include whether the biomass has been acclimated to the contaminants under study before the trial runs, whether the contaminant was added as a single or multiple substrate feed, and whether the process was operating at steady-state conditions. Other considerations in the process evaluation include variable hydraulic or solids retention times, and the use of realistic concentrations. Studies wherein feed concentrations of metals or organics are several hundred mg/L are not realistic compared with the situation at full-scale treatment plants.

The database with respect to concentrations and removals of trace contaminants in processes other than activated sludge and primary clarification is sparse. In addition, there are scant data on internal recycle streams (e.g. dissolved air flotation subnatant, incinerator ash pond water, centrate from centrifuges, elutriates, etc.), and the impact of these recycle streams on plant performance.

Modelling of the removal mechanisms in wastewater treatment plants is still at a relatively early stage. A model for volatilization has been developed for diffused aeration systems, but it does not distinguish between coarse and fine bubble systems. A model for surface aeration volatilization incorporated with the other removal mechanisms has not been developed, although Roberts et al (1984) have proposed a model for volatilization only. The model by Roberts et al (1984) relates the oxygen mass transfer coefficient (K_La) to the stripping rate constant of trace organics from water, but this may not be applicable for all volatile organics. The concept of using lyophilized biomass in biosorption studies appears promising, but additional data on flocculating and settling properties are required to confirm that it behaves like viable biomass. Additional procedures may need to be developed to confirm that lyophilized biomass has identical adsorptive properties with enzymes is nearly impossible, no mechanistic model has been developed. Some kinetic rate equations have been developed.

The database concerning variability of trace contaminants in wastewater treatment influents and effluents is extremely limited (i.e. metal concentrations in raw wastewater only). No attempt to define the dynamic response characteristics of treatment plants to fluctuating trace contaminant levels was noted.

Although some data have been established for contaminant levels in industrial wastewaters [e.g. Treatability Manual (EPA, 1980), the Report to Congress (EPA, 1986)], additional data characterizing industrial waste discharges are needed, particularly for improving models for sewer use management such as HAZPRED and SUBAS. Effective control of trace contaminant loadings at source by sewer-use bylaws aimed at trace contaminants, particularly organic compounds, needs a means to define the major contributors of trace contaminants to the sewer collection system.

7.3 Interpretation

More and more effort is being expended to characterize wastewater influents, effluents and sludges in municipal treatment plants. These data are generally the result of a single 24-hour composite or grab sample, and while these may be adequate for regulatory or water quality survey purposes, they provide little useful information about contaminant fluctuations within a plant, or about variations in plant removals efficiencies. Data from the EPA (1982b) 30-day study indicate that while removal of conventional parameters such as BOD_5 and TSS may be consistently high, concurrent removal efficiencies of trace contaminants can be highly variable. Contaminant variability relative to the mean value has been shown to be at least as large in the effluent as it was in the influent.

There is very little information on which to evaluate the dynamic response characteristics of biological treatment to trace contaminant concentration fluctuations. Oliver and Cosgrove (1974) found that pulses of total zinc in raw wastewater were greatly reduced by biological treatment. Soluble zinc levels did show some response in the effluent as a result of the influent perturbations. In the limited data provided by the 30 day study (EPA, 1982b) and the 40 POTW study (EPA, 1982a), there were some contaminants with highly correlated influent and effluent concentrations, However, these were not consistent between the two studies with one or two exceptions. It is possible that at a specific plant, some contaminant concentrations are highly correlated before and after treatment. Intensive sampling programs would be required to confirm this postulate.

At the present time, it cannot be determined if there is a significant degree of variation in the concentrations of trace contaminants in a specific treatment plant effluent; thus, it cannot be established whether the variability, if it exists, is a response to fluctuations in the raw wastewater concentrations, or whether the effluent variability may result from other factors such as internal loadings from recycle streams or the manner in which processes are operated (e.g. SRT, aeration rate, etc.). Contaminant variability in the effluent may be reduced by optimum control of the biological treatment process or by improved management of internal recycle streams. If these control procedures fail to reduce the effluent variability, then the remaining counter-measure is implementation of sewer-use bylaws and/or pretreatment programs aimed specifically at trace contaminants, including trace organic compounds.

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